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FEASIBILITY STUDY OF USE OF MOLTEN SALT TECHNOLOGY FOR PYROLYSIS OF SOLID WASTE

BATTELLE-PACIFIC NORTHWEST LABORATORIES

PREPARED FOR
NATIONAL ENVIRONMENTAL RESEARCH CENTER

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Information obtained in the laboratory studies was used to prepare conceptual process and equipment flow diagrams for evaluation of process economics. The processing of municipal refuse in molten sodium carbonate was found to be technically feasible but economically impractical, pending development of a simplified ash removal process. Use of molten salts is recommended for processing of hazardous materials because complete destruction of wastes is obtained in the molten salt.

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This publication provides the results of a study to determine the feasibility of using molten salt technology for pyrolysis of solid wastes. The study also evaluated the process as a method for cementing combustible solid waste to a combustible gas. In addition, because the process completely destroys the waste subjected to the molten salt, the process may provide a good method for processing selected hazardous waste.

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National Environmental
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ABSTRACT

The nation's current solid waste management and energy problems have prompted the Federal Government to evaluate alternative methods for conversion of solid waste to a useful energy source. The subject of this report is an evaluation of a molten salt process for conversion of combustible solid wastes to a combustible gas.

Laboratory scale studies were conducted on the pyrolysis of a typical refuse mix in molten sodium carbonate. Gasification of the char that resulted from pyrolysis of solid waste was studied at different conditions using steam, air, and oxygen as the gasification agent. The effects of contaminants that are introduced to the molten salt during processing of municipal refuse on gasification rates and corrosion were determined. Methods for ash removal from the molten salt were investigated. The value of products the molten salt system was determined.

Information obtained in the laboratory studies was used to prepare conceptual process and equipment flow diagrams for evaluation of process economics. The processing of municipal refuse in molten sodium carbonate was found to be technically feasible but economically impractical, pending development of a simplified ash removal process. Use of molten salts is recommended for processing of hazardous materials because complete destruction of wastes is obtained in the molten salt.

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CONCLUSIONS

The following conclusions are based on the results of the laboratory investigations, flowsheet development work and the economic analysis of the molten salt pyrolysis technology for processing solid waste. All experimental work was conducted using sodium carbonate as the typical molten salt.

- The molten salt process was proven to be technically feasible as a method for processing solid waste and procucing intermediate Btu gas, but not economically feasible when compared to alternative processes.

- Complete and rapid destruction (pyrolysis) of carbonaceous materials in municipal refuse is obtained in molten sodium carbonate at 900°C with an intermediate Btu gas (about 500 Btu/ft), producing a char residue.

- Char residue from pyrolysis of municipal refuse is combusted to produce sufficient energy to make the process autothermal; air or oxygen may be used for combustion of the char.

- A synthesis gas is produced from a reaction of the char with steam and is pseudo first order with respect to the carbon concentration in the molten sodium carbonate.

- A quantitative reaction of the char in the molten salt with air and oxygen produces mainly carbon monoxide; over 2 wt% of the carbon is unreacted and remains in the molten salt.

- Regardless of the method of feeding refuse (surface feeding or submerged feeding), the gas produced by pyrolysis of municipal refuse in molten sodium carbonate is essentially free of tars and oils.

- Up to 30-mole % sodium hydroxide is produced by purging the molten sodium carbonate with steam after complete reaction of the char.

- Gas cleanup requirements are minimal since tars and oils are not produced when municipal refuse is processed in a molten salt.

- Recovery of valuable solid byproducts, such as aluminum, is not possible by processing in a molten sodium carbonate; aluminum oxidizes rapidly in the molten sodium carbonate with traces of air present.

- Since filtration of the molten sodium carbonate was unsuccessful, aqueous processing of the molten salt is required for ash removal.

- Corrosivity of the molten salt is a major problem in design of process equipment. No metallic material was found to be satisfactory for containment of the molten salt system. Literature sources indicate that a refractory material, high purity alumina, is a suitable containment material.

- Capital costs are estimated to be $60,700 and $43,800/ton/day of solid waste using air as the process oxidant for 200 and 1000 tons/day plants respectively.

- Revenue is estimated to be $7.03/ton of solid wastes at a gas price of $1/10^6 Btu for all capacity plants.

- The process will not be economically competitive with other resource recovery systems until less costly construction materials can be identified to eliminate potential corrosion problems.

- The process appears attractive for processing hazardous materials and should be evaluated experimentally for this purpose.

RECOMMENDATIONS

Results of the study on molten salt pyrolysis of municipal refuse lead to the following recommendations:

- Molten salt processing is recommended for processes where complete destruction of carbonaceous materials is required. It is particularly attractive for destruction of noxious fumes and of waste pesticides and herbicides with low ash content. Destruction of waste nerve gases and biological warfare agents would be complete in a molten salt media such as sodium carbonate, and destruction of waste explosives may also be possible.

- Large scale processing of municipal refuse in molten sodium carbonate is not recommended due to the complicated ash removal requirements, the expensive materials required, and associated high capital and operating costs. However, specialized application to small scale processing of municipal refuse in remote areas under special circumstances may be economically justifiable.

- The technical and economic feasibility of using this process as a method for destruction of hazardous wates should be evaluated. Laboratory experiments should be conducted to confirm the potential advantages of the process over other thermal destruction techniques for the processing of hazardous wastes.

FEASIBILITY STUDY OF USE OF MOLTEN SALT TECHNOLOGY
FOR PYROLYSIS OF SOLID WASTE

(Contract No. 68-03-0145)

to

National Environmental Research Center
Environmental Protection Agency
Cincinnati, Ohio 45268

INTRODUCTION

GENERAL BACKGROUND

The Federal Government has recognized two major problems facing the nation today: solid waste management and an energy shortage. Among the steps being taken to alleviate these problems is the study of the possible use of molten salt technology as a method of converting solid wastes to a useful fuel. This could help solve both the solid waste and the energy problem. The program discussed here was designed to investigate the technical and economical feasibility of this approach.

The emergence of solid waste as a national problem in environmental management is clearly recognized by governmental and public sectors within the United States. Present annual generation of solid waste within the U.S. exceeds 200 million tons and future quantities are projected to increase dramatically.[1] Historically, society has been content to dispose of solid waste by moving it to landfill or open dumping sites and by burning large portions of the combustible fraction of the wastes. Such practices significantly contribute to environmental pollution and make waste of resource values possessed by the solid wastes. In addition, national costs for solid waste collection, processing and disposal are factors contributing to a solid waste management problem which warrants many improvements.

The government has taken action to solve these problems by enacting legislation, including the Solid Waste Disposal Act of 1965, the Resource Recovery Act of 1970, and the National Materials Policy Act of 1970. This legislation has clearly pointed out the necessity of recovering useful energy and materials from solid waste,[2] recognizes that the 200 million tons/year of solid wastes are becoming an increasingly valuable national resource, and identifies development of a system for economic reuse of solid wastes as a national objective.

A second national problem is the energy crisis which has been brought about by:

- The accelerated increased demand for power
- The air pollution problems brought about by out-dated power plants with limited air control equipment.
- Limited development of new petroleum and natural gas fields due to the high exploration and development costs.

Incineration, a controlled combustion process, offers one method of reducing the volume of solid wastes. The combustible materials are reduced over 95 wt% by conversion of the combustible portion of the solid waste to water and gases which are released to the atmosphere. The overall weight of typical solid wastes containing combustible and inert components is reduced 80 to 90% by incineration. A major limitation however, is that large, bulky, combustible wastes, such as tree stumps, logs, large furniture, tires, mattresses, and demolition lumber, require special handling equipment if they are to be processed in municipal incinerators. If they are not incinerated, these items add significantly to the amount of land required for disposal.

Another major limitation of incineration is the high capital cost associated with such installations. Stack-gas cleaning equipment required to meet air pollution standards accounts for a significant fraction of the total incinerator cost. However, pyrolysis processes and two-stage incineration processes have the potential of being operated without electrostatic precipitators, bag filters, cyclone separators, and other gas-cleaning equipment. For this reason they are attracting considerable attention as waste reduction processes.

Carbonaceous waste materials can be decomposed by two processes: 1) direct combustion (incineration) in a supply of oxygen or 2) pyrolysis in the absence of oxygen. Both processes can be carried out in a molten salt bath. The end products of complete, direct combustion are carbon dioxide and water, while the end products of pyrolysis are char and gaseous hydrocarbons. However, metallic and mineral materials present in the waste are retained by the salt in both processes, unless vaporized at the salt operating temperature. The char remaining from pyrolysis can be removed by cooling, dissolving and filtration from the molten salt or by reaction with an oxidizing agent.

Before this molten salt program was conducted the potential advantages of the molten salt process were considered to be:

- Fly ash and other particulates would be wetted and retained by the molten salt.

- Noxious contaminants such as sulfur compounds and trace metals would be retained in the molten salts, thus eliminating the need for expensive stack gas cleanup systems.

- Liquid heat transfer for the pyrolysis of the waste would make the system very efficient from a heat utilization standpoint.

- Hazardous chemicals such as pesticides and herbicides could be efficiently destructed.

- When compared to other nonslagging pyrolysis systems, ash removal would be simplified by using salt as a molten grate.

- Solid wastes would be converted to a valuable heating gas similar to that produced by coal gasification.

- Solid residues could be recovered from the molten salt process, thus providing revenue and reducing operating costs.

DESCRIPTION OF RESEARCH PROJECT

The potential advantages of this process were sufficient justification for the United States Environmental Protection Agency (EPA) to contract with Battelle-Northwest (BNW) to conduct this study under contract number 68-03-0145; work started on June 30, 1972. The objective of this program was to perform laboratory experiments, and technical and economic evaluations of the molten salt pyrolysis and combustion processes as a method of converting solid waste to a salable energy resource. Specifically, it was designed to delineate the advantages and disadvantages of such a pyrolytic processing scheme as it relates to current and future solid waste disposal and reclamation technology.

In order to meet these objectives, the following major tasks were conducted.

- Define and evaluate the feasible operating temperatures and pressures, waste feeding methods, operating and control parameters, effect of melt contamination, and the potential for processing and reclaiming municipal refuse and other specialized wastes.

- Define and evaluate ash residue removal methods and equipment, and recirculation methods and equipment.

- Define and evaluate characteristics of the pyrolytic gases and solid residues.

- Conduct a preliminary technical and economic analysis of the molten salt technique in terms of its potential for processing solid wastes.

The program conducted by Battelle-Northwest was designed to build on the results of similar BNW programs conducted in this field and to determine if any further work, such as pilot plant studies, should be conducted in this area. The following is a description of each task conducted in this study.

Task I - Continuous Process Studies

The objective of this task was to determine the operational characteristics of a molten salt system for processing typical municipal wastes. An experimental program was designed to establish:

- the range of feasible operating parameters
- the waste feeding method
- preliminary operating and control parameters
- the effect of melt contamination.

Studies were performed in a 4-in. diameter Inconel reactor. A sodium carbonate melt was used to determine char gasification rates at temperatures between 870 and 1000°C, and steam pressures of 0.25 to 5 atm. Char burning rates with air and pure O_2 were determined in the same temperature range, while rates of char disappearance for O_2-steam mixtures were determined for one mixture of O_2-steam. The effect of the superficial steam velocity on gasification rates was determined at a single temperature and pressure. The effect of melt height at a single steam velocity, temperature and pressure was determined. Gas evolution rates and composition were determined in all the experiments. Gas chromatographic analysis was used to identify the products of char gasification.

Two methods were investigated for solid waste feeding. In one method, surface feeding, pyrolysis products did not contact the molten salt before release from the reaction chamber; in the other method, submerged feeding, the pyrolysis products contacted the melt before release from the reaction vessel.

Task II - Ash Removal Studies

The objective of this task was to determine the properties of the ash-molten salt slurry to allow evaluation of ash removal systems. Information was gathered to ascertain:

- required melt recirculation equipment
- equipment requirements for ash removal
- feasibility of large scale ash removal.

Attempts to determine ash settling rates were hampered by the solubility of the ash in the melt. Filtration of the melt at 900 to 960°C was attempted and failed due to filter plugging.

Task III - Product Evaluation

The objective of this task was to characterize the gaseous and solid products from a molten salt system for processing solid waste. Data from Task I on the composition of the gas stream from individual process components was assembled and analyzed as part of alternate processing systems. The net energy production and processing rates for feasible processing methods was then determined. The volume, composition, and calorific content of the gas products from alternate processing systems were then specified; tars and oils were not present in the product gas stream.

Task IV - Economic Analysis

The objective of this task was to estimate the operating and capital costs for both a 200 and 1000 tons/day molten salt facility. Published data and data previously developed by BNW was used to determine the costs and potential revenues for all subsystems and process streams other than the molten salt system. An engineering flow diagram defining the required processes, equipment and operating parameters was developed and used as the basis for this study, and major equipment items were identified. The system included the following subsystems.

- Storage, segregation, shredding, and materials handling front end subsystems
- Molten salt pyrolysis/incineration system
- Pyrolysis gas handling system
- Solid residue handling systems.

The potential revenues for the pyrolysis gas were estimated using information developed in the Kennewick Pyrolysis/Incineration Program conducted for the City of Kennewick, Washington and the EPA in addition to other published data.[3,4,5,6] Municipal solid waste was the only feed stock that was evaluated in the economic analysis.

EXPERIMENTAL EQUIPMENT AND METHODS

The design and fabrication of equipment used in the study is described in the following discussion. Materials used for equipment construction are identified, while experimental procedures are described in the section following the description of equipment design and fabrication.

DESIGN AND FABRICATION OF EQUIPMENT

Equipment was designed and constructed for the char gasification studies (described below), and equipment available from another program was installed for the study of submerged feeding methods. Ash removal and melt contamination studies were conducted using available equipment including pot furnaces, controllers, and alumina crucibles.

A flow schematic of the equipment used in the char gasification studies is shown in Figure 1. The water reservoir was a 2-liter graduated cylinder. Water was pumped from the reservoir with a Lapp Pulsafeeder, LS-10, that had a pumping rate continuously variable between 0 and 40 ml/min. The steam generator was a 2-in. Sch 40 stainless steel pipe that was 3 ft long and lagged with heating tape that had a heating capacity of 1152 watts. The superheater consisted of 20 ft of 3/8-in. stainless steel tubing coiled inside a Lindberg Hevi-Duty tube furnace. Air, O_2, and N_2, if required, were metered individually through 1/4-in. stainless steel tubing into the superheater. Steam and any combination of gases could be used to gasify the char. The gases passed through 3/8-in. tubing from the superheater to the molten salt reactor and a stainless steel condenser cooled the gases from the reactor and removed moisture which was collected in a stainless steel condensate receiver. A Grove[a] back pressure regulator with a 0 to 150 psi range was used to keep the pressure in the reactor constant at the desired value. All gases passed through a wet test meter to measure the quantity of gas generated during gasification and pyrolysis of the refuse. The experimental equipment is shown in Figure 2.

The molten salt reactor used in the char gasification studies is shown unassembled in Figure 3 and assembled in Figure 4. The shell of the reactor was fabricated from 4-in. Sch 40, Inconel 600 pipe and pipe caps. A 1/8-in. metallic asbestos gasket was used to seal the two flanged sections of the reactor. Gas was admitted near the bottom of the reactor through a sparge ring constructed from 1/2-in. Inconel 600 pipe. Holes of 1/16-in. diameter were spaced 1/4 in. around the top of the ring with 4 1/16-in. drain holes on the bottom of the ring.

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[a] Trademark

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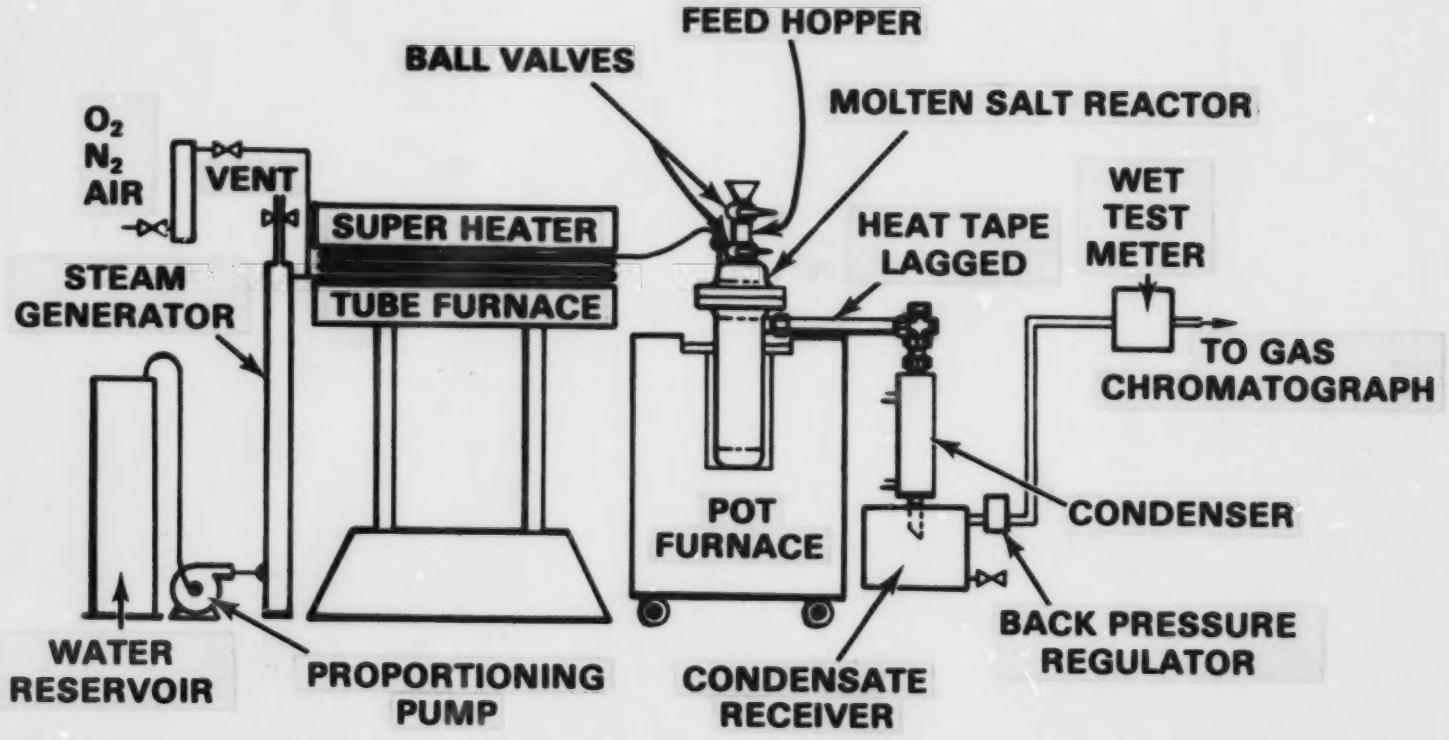


FIGURE 1. Gasification Equipment Schematic

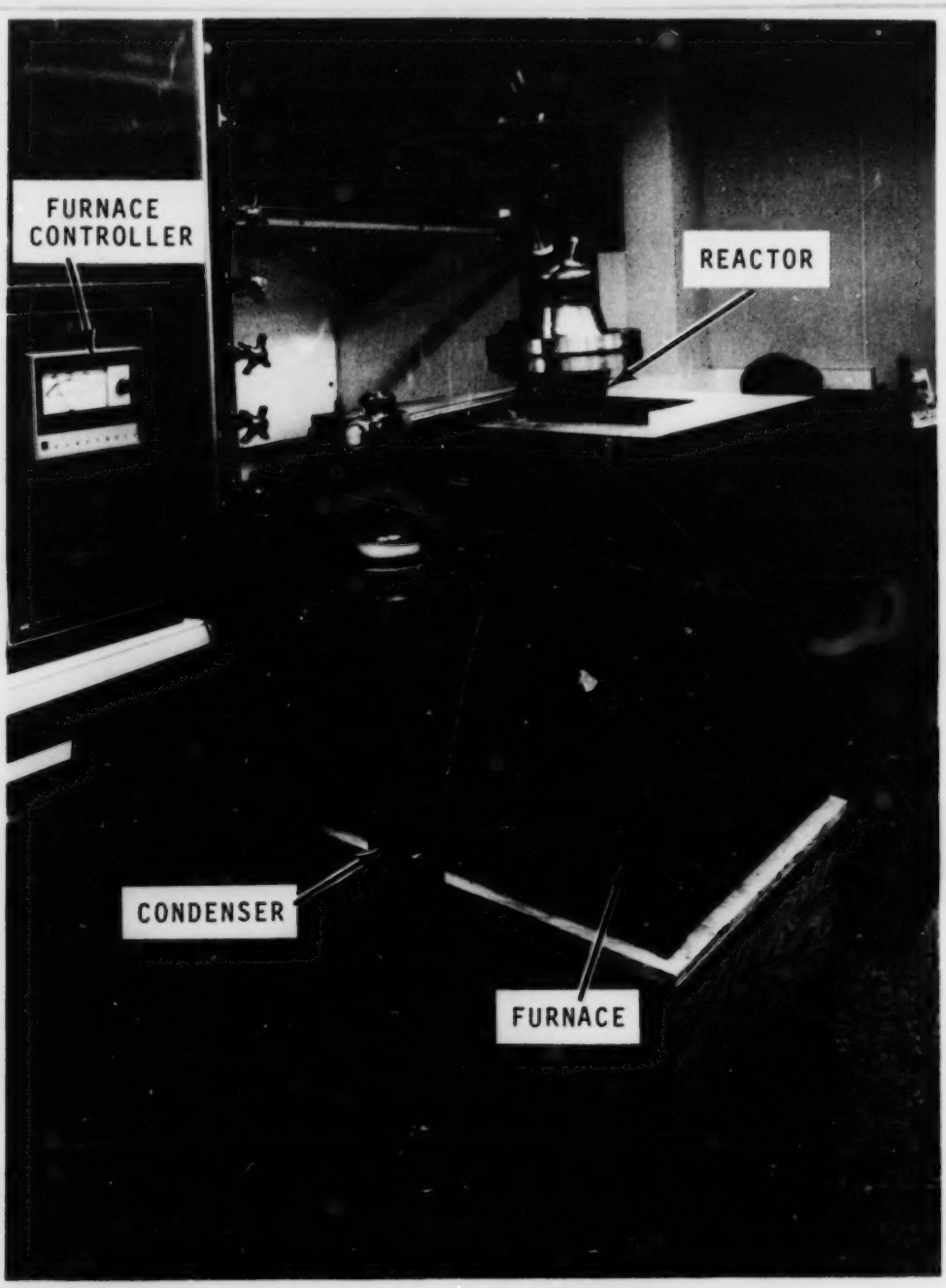


FIGURE 2. Molten Salt Gasification Equipment

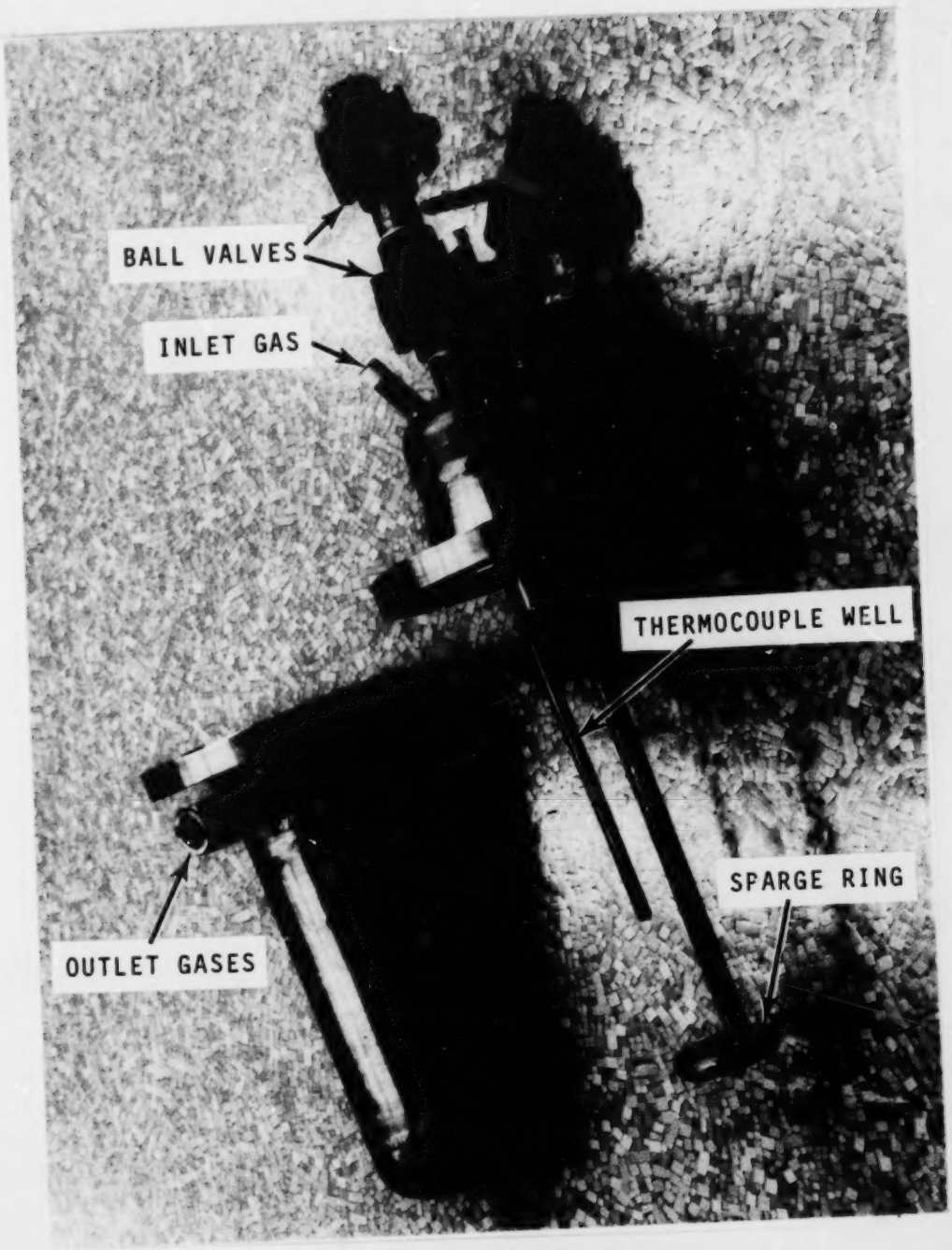


FIGURE 3. Unassembled Reactor

FIGURE 4. Assembled Reactor

An air lock arrangement was used to charge material into the reactor and two ball valves enclosed the charging chamber. With both valves closed, the upper valve was opened to admit the charge and then closed, the chamber was then pressurized to equal the pressure in the reactor and the lower valve was then opened to drop the charge in the reactor. The two 1-in. ball valves and chamber shown in Figures 2, 3, and 4 were later replaced by 1-1/2 in. valves and a 2-ft pipe for a chamber so that the size of the charge could be increased. The pressure relief valve was added to guard against inadvertent over-pressurization of the molten salt reactor.

The assembly for the study of submerged feeding methods is shown prior to addition of heating elements in Figure 5. The scrubber and pyrolysis chamber were made from 4-in. Sch 40, Inconel 600 pipe. A 1-in. Inconel 600 pipe was used to join the scrubber to the pyrolysis chamber and provide a means for gas exhaust, while providing gas lift recirculators a means of salt recirculation in each chamber. The scrubber was packed with 1/4-in. Inconel 600 Raschig rings to a point about 2 in. below the recirculator discharge. Figure 6 shows the unit ready for operation. Material was charged to the pyrolysis chamber through an air lock as shown in Figure 6. Gas exited from the scrubber into a wet test meter and was collected in bags for analysis in the gas chromatograph.

On-line analysis of the reactor off-gas was used for the char gasification studies. Gas samples were collected in 20 liter bags during the study of solid waste feeding methods. The gases were analyzed for H_2, N_2, O_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6 using a Hewlett-Packard Model 7624A gas Chromatograph; the time required for each gas analysis was about 10 min. Sample injection was via a heated gas sampling valve equipped with 0.5 cm^3 sample loops. The drierite column removed all moisture from the gas sample. A schematic of the sample flow through the gas chromatograph is shown in Figure 7.

The apparatus shown in Figure 8 was constructed to study the filtration characteristics of molten salt ash slurries. The sintered stainless steel filter, 2-in. square and 1/4-in. thick with a mean power diameter of 5μ, was welded into a 2-in. square duct which was made with Swage-lok fittings and the entire assembly was sized to fit inside a 6-in. diameter pot furnace. The molten salt container was a 2-in. stainless steel pipe with the top end open to allow addition of the slurry and observation of slurry level changes. The filtrate receiver was made from 2-in. stainless steel pipes with caps welded to both ends and with tubing connections to the top cap as shown in Figure 8.

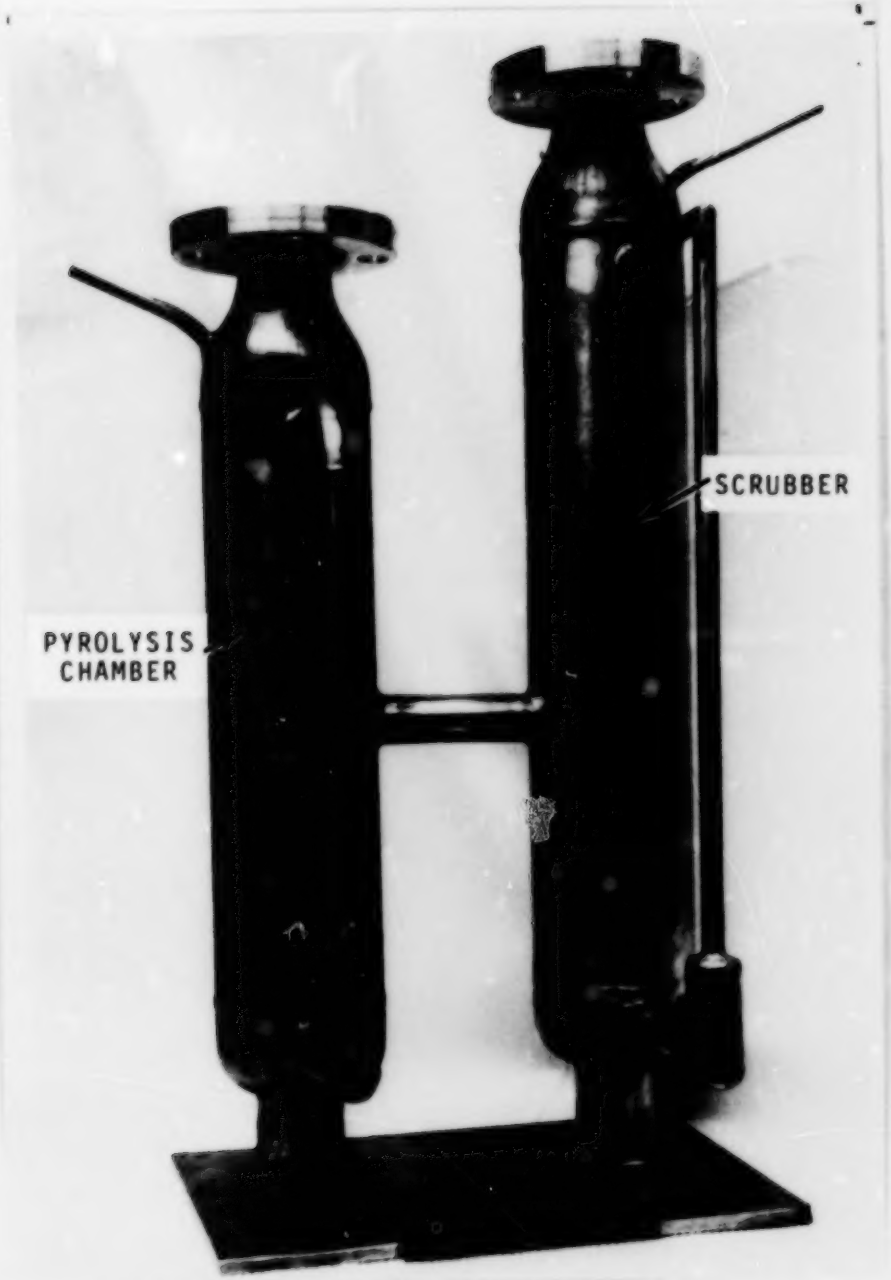


FIGURE 5. Molten Salt Pyrolysis Reactor for Submerged Feeding Studies

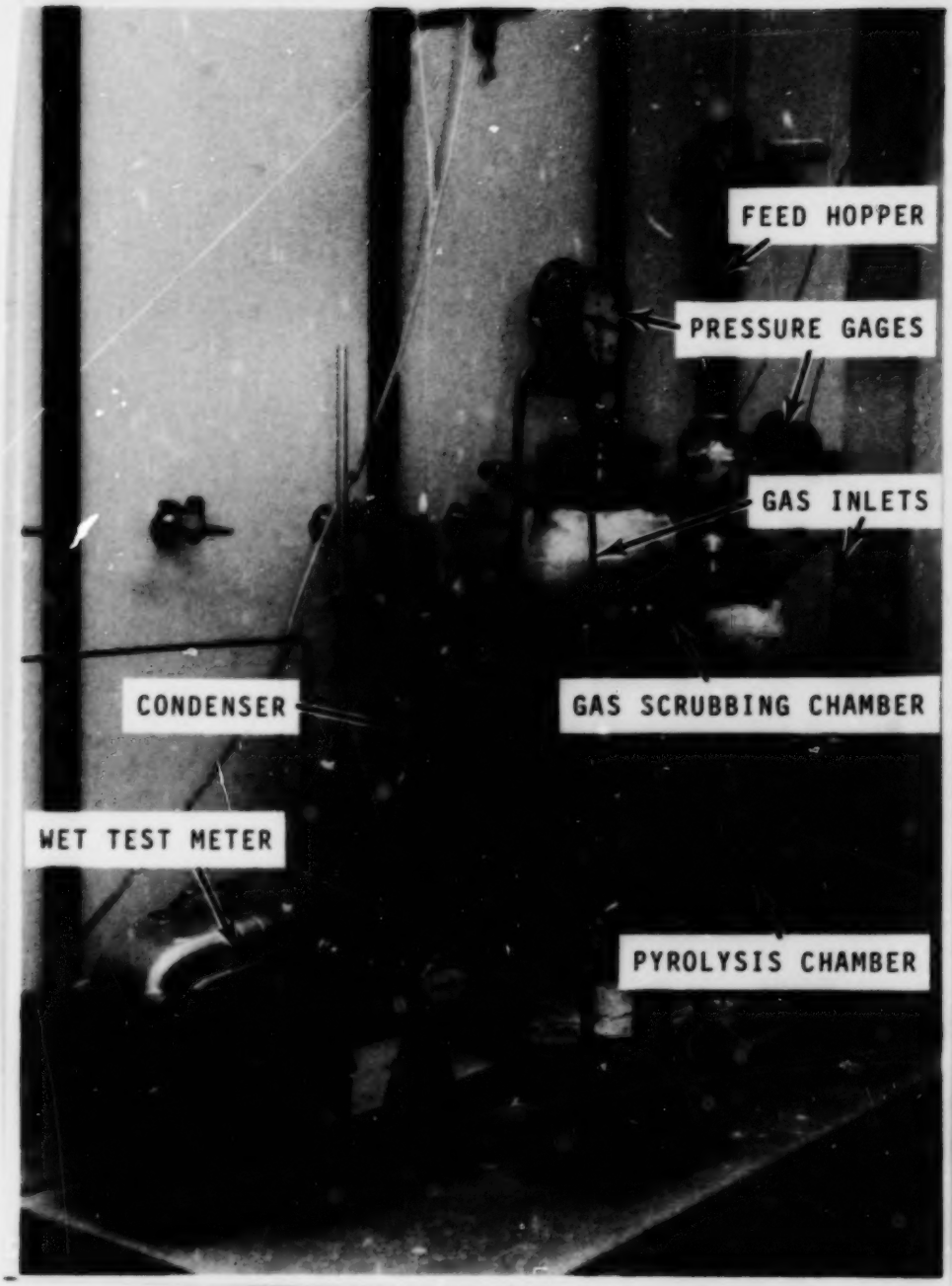


FIGURE 6. Equipment for Submerged Feeding Experiments

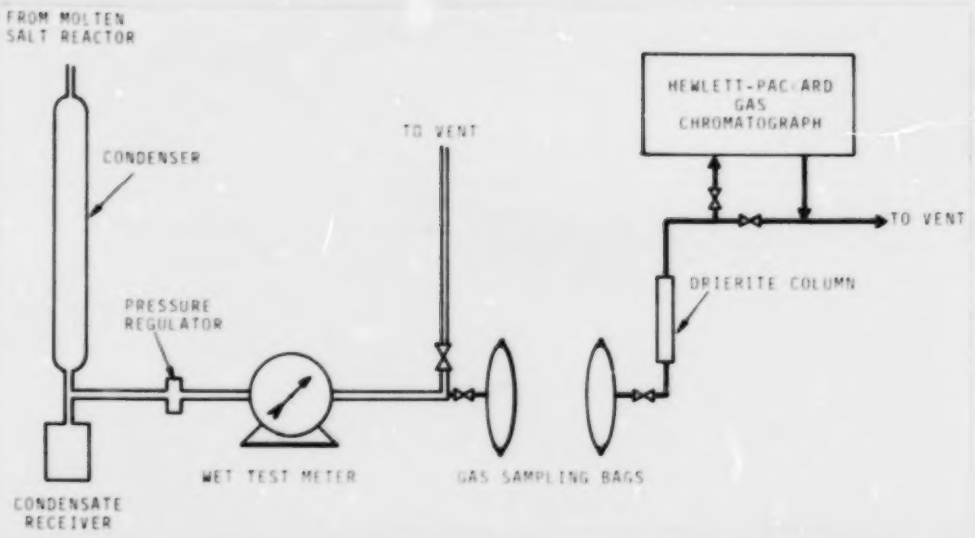


FIGURE 7. Schematic of Sample Train

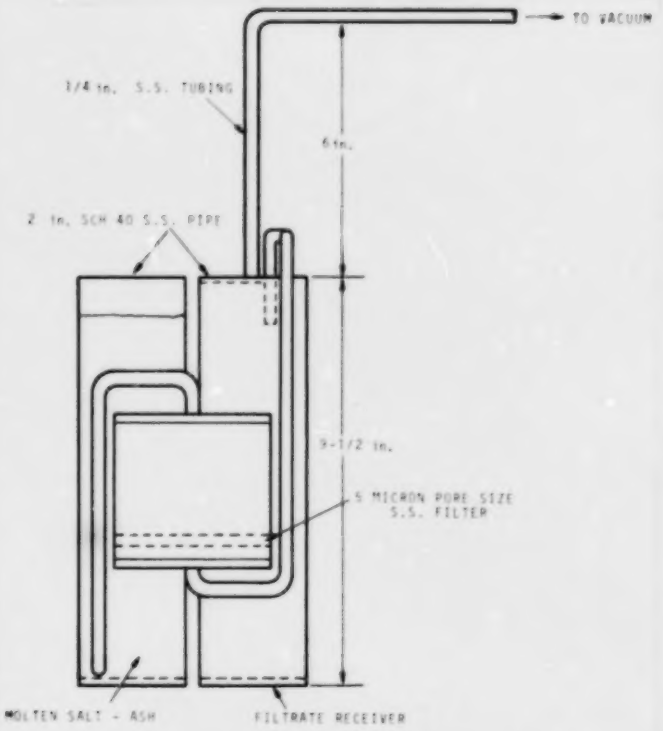


FIGURE 8. Molten Salt Filter

EXPERIMENTAL PROCEDURES

Char gasification studies were conducted to determine the kinetics of gasification. Independent variables that were studied included temperature, pressure, melt level, ash concentration, and superficial linear velocity. Char was prepared by the pyrolysis of municipal refuse at 800°C. (The equipment used is shown in Figures 1 through 4 and described above.) The procedure used in the gasification runs was as follows. Reagent grade sodium carbonate was charged to the reactor to give the desired molten salt operating level. Usually, a 2400 g charge of Na_2CO_3 was used to give a molten salt depth of 6 in. After charging the salt to the reactor, the pot furnace temperature was set at the desired temperature. A nitrogen purge through the salt was maintained at about 300 ml/min during salt heatup and melting. All lines to the reactor were heated to 400°C. The steam superheater was controlled at 500°C.

With the steam generator vent valve open and power to the heating tape, the proportioning pump was started to deliver the required steam flow for the gasification run. Flow from the pump was variable between 0 and 40 ml/min. Steam was vented for about 1 hr prior to initiation of flow to the reactor to assure a constant liquid level in the steam generator, and, therefore, a constant steam flow. Steady state operation of the steam generator was determined by temperature measurements at different levels in the steam generator. Steam flow to the reactor was initiated by closing the vent valve and opening the valve to the steam superheater. Flow of other gases (air, O_2, N_2) was started just prior to the initiation of steam flow. Pressure drop measurements between the steam generator and the superheater were taken prior to initiation of steam flow to assure that no back flow of molten salt in the lines occurred. Steam flow was determined by measuring the water volume in a graduated cylinder at the start and end of a run.

Freshly melted Na_2CO_3 was purged with steam for 15 to 30 min prior to the addition of char. A considerable amount of CO_2 was evolved during this conditioning stage. It was noted that early in the gasification run the melt was recarbonated, while late in the run, after nearly complete char reaction, CO_2 evolution was noted. Melt conditioning was used throughout the study where steam was used as the gasifying medium. Data was adjusted to account for the CO_2 absorption-desorption phenomenon.

Char was added to the charging hopper which was purged with N_2 to eliminate air. About 60 g of char could be added in a single dump; between 100 and 150 g of char were used for each

run. After char addition to the melt, flow of gases was initiated as required for the experiment.

After significant generation of gas was noted by flow through the wet test meter, in-line sampling of the gas was started. A complete analysis of the gas was obtained about every 10 min.; a stop watch was used to time the runs. Significant gas generation usually started 3 to 4 min after initiation of flow of the gasifying medium. The volume of gas generated was recorded at 1-min intervals after initiation of the experiment. The run was continued until the net gas generation decreased to less than 1 liter/min.

After the ash concentration in the molten salt reached 8 to 10% by weight, the molten salt was ladled from the reactor into a stainless steel tray where it was allowed to freeze and cool. The cooled reactor was flushed and cleaned with water. The ash was recovered from the salt cake by dissolution of the Na_2CO_3 and filtration of the ash residue.

Two feed addition methods were studied during the course of the study: 1) surface feeding in which the vapors were not forced to contact the salt, and 2) submerged feeding in which the vapors were forced to contact the salt prior to venting from the reactor. Submerged feeding experiments were conducted with and without circulation of molten salt through the gas lift recirculation arms.

Surface feeding studies were conducted in the equipment shown in Figures 1 through 4 and described in the previous section. A 2400 g charge of Na_2CO_3 was added to the reactor and melted, and a 300 ml/min N_2 purge was maintained throughout the heating period and subsequent feed additions.

Municipal refuse was formed into pellets that weighed up to 40 g and could be added to the feed hopper. Care was taken to maintain the same ratio of refuse components in the pellets. The feed hopper was purged with N_2 before the lower valve to the reactor was opened to drop the charge onto the molten salt. Evolved gases and vapors were passed through a condenser to collect water, tars and oils, and through a wet test meter to determine the volume of noncondensibles. Gas samples were collected in 20-liter bags for analysis on the gas chromatograph. Gas volume readings on the wet test meter were recorded every 30 seconds after addition of the municipal refuse to the molten salt reactor.

Submerged feeding experiments were conducted in the equipment pictured in Figure 6. Sodium carbonate was added to the incinerator leg of the apparatus in sufficient quantity (6600 g) to fill both the scrubber and incinerator to a level just above the connecting pipe. A nitrogen purge was maintained through the gas lift recirculators during melting of the salt.

Refuse pellets were added to the incinerator leg of the apparatus through the feed hopper as was done in the surface feeding experiments. Gases and vapors from pyrolysis of the refuse passed through the molten salt in the scrubber leg and exited to a condenser, wet test meter, and a sample bag, identical to the off-gas system used for processing the gas in the surface feeding experiments. Refuse additions were made with and without a nitrogen purge of the gas lift recirculators. Gas volume readings on the wet test meter were recorded every 30 seconds after additions of the refuse pellets.

Procedures used for molten salt filtration studies are presented with the results of those studies in a subsequent section. Equipment used for a portion of the study is shown in Figure 8. The entire apparatus is sized to fit inside a 6-in. diameter pot furnace. Ceramic filters made from alumina and magnesia were also used to filter the molten salt.

EXPERIMENTAL RESULTS

The experimental program was designed to determine char gasification rates, feed methods, the effect of melt contamination, and methods for ash removal. Results of these studies were used to determine product values and operating parameters, and to develop flowsheets for determination of economic feasibility of molten salt processing of municipal refuse.

Shredded municipal refuse obtained from the city of Vancouver, Washington, was characterized for use as the feed material for the molten salt studies. A sample weighing 160 lbs was sorted to determine the average composition shown in Table 1.

TABLE 1. Vancouver Refuse Composition

Component	Wt%
Paper	38.5
Rubber and leather	2.0
Wood	5.3
Metals	7.0
Aluminum	0.6
Plastic	1.7
Cloth	5.7
Fines (mostly paper, some dirt & glass)	39.2
Food	0.1
Glass	all with fines
Yard waste	0.1

An ultimate and proximate analysis was obtained on the combustible portion of the municipal refuse from an independent testing laboratory recommended by EPA. Results obtained from the laboratory are shown in Table 2.

TABLE 2. Proximate and Ultimate Analysis of Vancouver Refuse

Ultimate Analysis	Wt%
Moisture	5.08
Carbon	45.91
Hydrogen	7.06
Oxygen	28.82
Nitrogen	4.19
Sulfur	0.10
Chlorine	0.32
Ash	14.18
CO_2	None detected
Proximate Analysis	
Moisture	5.08
Volatile at 950°C	80.74
Ash	14.18
Heat content	2304 Btu/lb

An inert molten salt, Na_2CO_3, was selected for use in the studies. Properties of Na_2CO_3 are shown in Table 3.[7]

TABLE 3. Properties of Na_2CO_3

Molecular weight	106.0
Melting point, °C	851
Viscosity at 900°C	2.99 cp
Density at 900°C	1.953 g/cc
Specific heat at 900°C	0.439 cal/g°C

Basis for the selection of Na_2CO_3 as the fused salt system was previous experiments conducted with fused salts for the destruction of radioactive solid wastes. Eight salt systems were investigated for the decomposition of the radioactive solid waste. They were:

- LiCl, 45% KCl
- KNO_3, 46% $NaNO_3$
- $K_2S_2O_7$
- $K_2S_2O_7$, 8% V_2O_5
- NaOH
- NaOH, 10% $NaNO_3$
- 25% K_2CO_3, 44% Li_2CO_3, 31% Na_2CO_3
- 22% K_2CO_3, 40% Li_2CO_3, 28% Na_2CO_3, 10% $NaNO_3$

For application to radioactive wastes, the KNO_3-$NaNO_3$ mixture proved to be the best "oxidizing" salt while the K_2CO_3-Li_2CO_3-Na_2CO_3 mixture was found to be the best "inert" salt. At 500 to 800°C, the molten nitrate salt reacted with, and oxidized most carbonaceous solids, even under an inert-gas blanket. The reaction rates observed were not excessive, but the alkali metal nitrate was consumed and converted to alkali metal carbonate. The salt could be regenerated by bubbling fumes of HNO_3 into the molten salt, but HNO_3 is relatively expensive. Cost of Li_2CO_3 and K_2CO_3 makes the use of the ternary carbonate system prohibitively costly for large scale application to municipal refuse; cost of Li_2CO_3 is about 50¢/lb while Na_2CO_3 costs about 1.5¢/lb.

Molten salt processing of municipal refuse was envisioned to consist of three major steps: 1) pyrolysis of the refuse in the molten salt, 2) combustion or gasification of the char that remained in the molten salt, and 3) separation of the ash from the molten salt. Studies on each of these steps and on the effect of melt contamination are presented in the following sections.

GASIFICATION STUDIES

Gasification studies were conducted on char prepared from the pyrolysis of the Vancouver refuse. Early in the program the refuse was pyrolyzed at 700°C in a batch, externally heated

retort. After the first five experiments, the pyrolysis temperature was increased to 800°C, since considerable distillation of the char produced at 700°C was noted to occur when charged to the molten salt. Pyrolysis of the refuse at 800°C was desirable to reduce the amount of pyrolysis that occurred in the molten salt so that the initial concentration of char in the molten salt was known more accurately.

Char produced by batch pyrolysis of the Vancouver refuse is shown in Figure 9, segregated into fractions produced from wood, paper, and cloth. The char that resulted from pyrolysis of paper and cloth was light and very friable, and had a calorific value of 8300 Btu/lb. The wood char was much less friable than the paper char and had a calorific value of 13,700 Btu/lb. The difference in the calorific values of wood and paper chars was directly attributable to the ash content of the two chars.

Pyrolysis at 700°C of 100 g of a typical mix of Vancouver refuse yielded 41.3 g of char, 26 g aqueous solution (100 g/liter total organic content), 5.4 g oil (114,000 Btu/gal) and 16.4 liters of gas. The average composition of the gaseous product as determined by gas chromatography is given in Table 4. Procedures and equipment used for determination of gas compositions are described in Appendix A.

TABLE 4. Pyrolysis Gas Composition

Gas Composition, vol%									
H_2	CO_2	C_2H_4	C_2H_6	O_2	N_2	CH_4	CO	C_3H_8	Btu/ft^3
12.4	34	0.6	2.1	2	4.5	15.1	25.0	0.5	348

Char gasification runs were made with steam, air, and oxygen as the gasifying agent. Independent variables studied with steam as the gasifying agent included temperature, pressure, superficial linear velocity, and melt level. In addition, the effect of ash buildup in the molten salt on the gasification rates was determined. In all, over thirty gasification runs were made in the study. The procedures used for the experiments are described in the Experimental Procedures Section.

Gas compositions, which were typical for all gasification runs with steam, are given in Table 5 for Runs 8, 9, and 12 as a function of time after initiation of the steam flow. The total gas production rate as a function of time after initiation of steam flow is given in Figures 10, 11, and 12 for the three runs. Also noted on the figures are the times when samples were withdrawn for gas analysis.

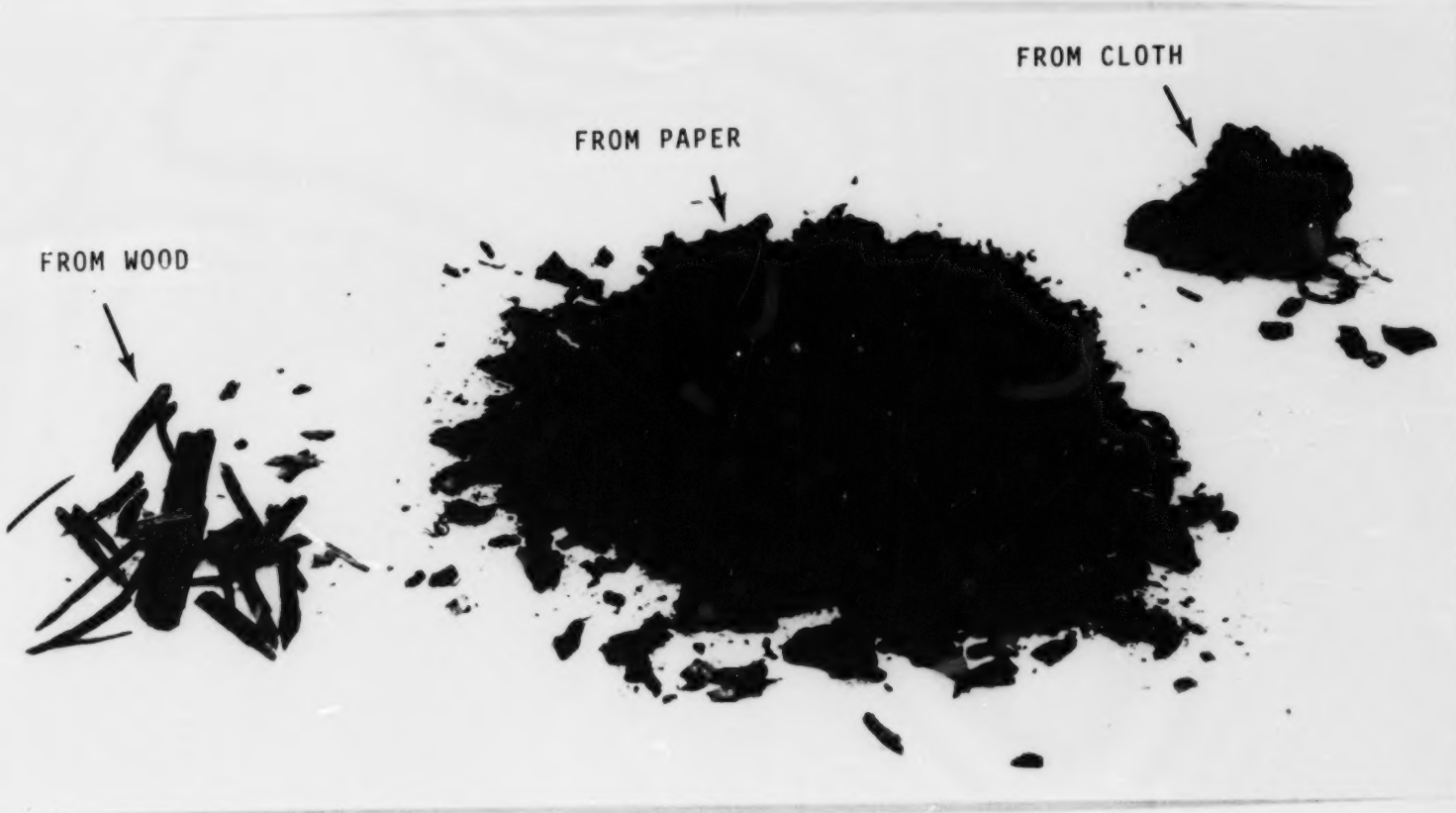


FIGURE 9. Char from Pyrolysis of Solid Waste

The data in Table 5 show that at the start of a run the hydrogen concentration is higher than can be accounted for by the water gas reaction:

$$C + H_2O \rightleftarrows CO + H_2 \qquad (1)$$

Further, the H_2 concentration cannot be accounted for by the shift reaction:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (2)$$

since initially the CO_2 concentration is low in comparison to the hydrogen, and later in the run it is comparatively high. Hydrogen can be consumed by the following reaction:

$$C + 2H_2 \rightarrow CH_4 \qquad (3)$$

This reaction is not favored at the conditions used in the experiments and, of course, cannot account for a high H_2 concentration. The data appear to be accurate in that the percentages total near 100%.

TABLE 5. Experimental Gas Compositions for Steam Gasification

Run	Sample Time min after start	Gas Compositions, vol% H_2	CO_2	N_2	CH_4	CO
8	8	~73	4.5	2.5	0.1	19.8
	14	56	29.1	5.0	---	11.7
	29	28	58.4	15.8	---	2.8
	40	24	53.5	24.1	---	1.4
9	3	~73	5.0	1.9	0.4	19.0
	13	56	16.4	1.6	0.2	25.5
	23	54	25.0	2.8	0.2	17.4
	33	47	38.5	7.0	0.1	8.0
	44	45	40.2	10.5	0.1	5.1
	59	45	44.5	16.2	---	2.8
	84	40	42.0	21.5	---	2.0
12	4	53	11.0	3.3	0.2	33.0
	14	54	32.0	5.0	0.2	11.0
	25	40	47.5	12.5	0.2	3.5
	36	40	43.5	16.0	0.2	2.5
	49	40	42.5	20.0	0.2	2.0

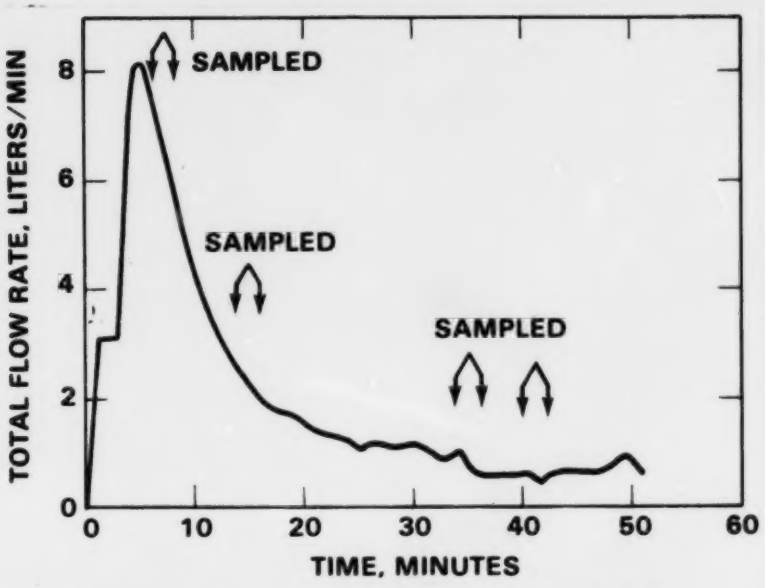


FIGURE 10. Total Gas Flow Rate for Run 8

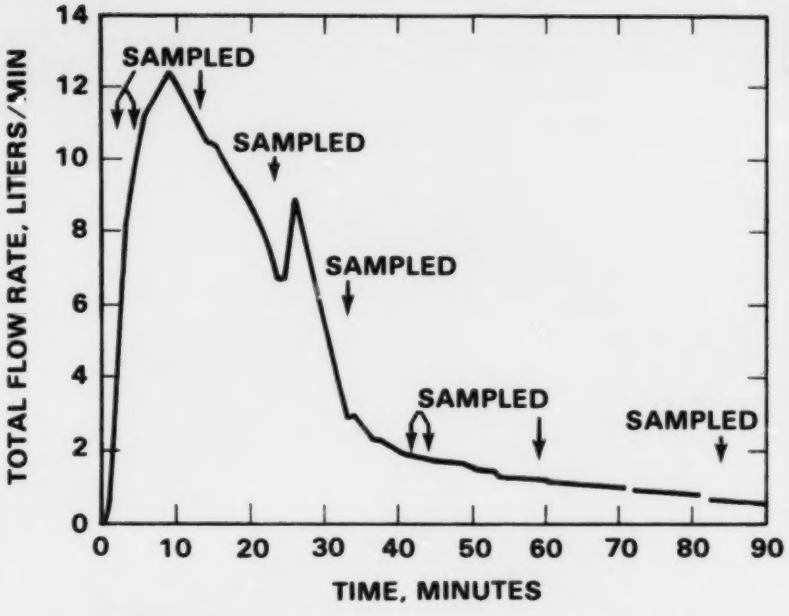


FIGURE 11. Total Gas Flow Rate for Run 9

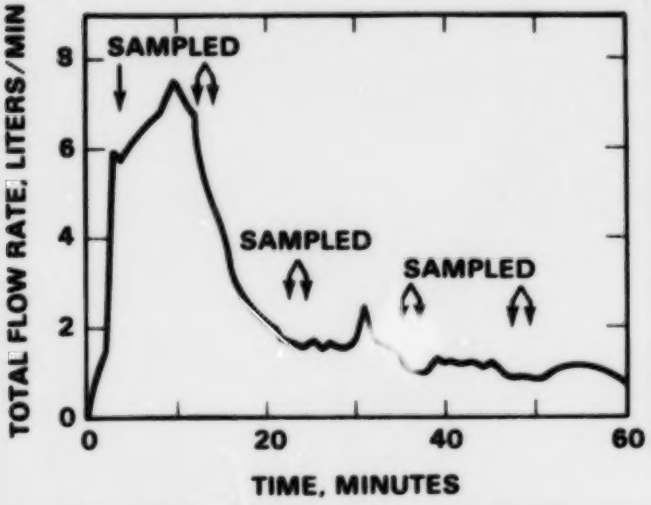


FIGURE 12. Total Gas Flow Rate for Run 12

The data in Table 5 also show that the CO_2 concentration increases markedly with time while the CO concentration decreases. The variations of H_2, CO, and CO_2 concentrations with time are shown in Figure 13 for Run 9. Also shown in the total flow rate of these three gases as a function of time after start of the steam purge.

The initial high hydrogen concentration did not occur in all runs, as evidenced by the data shown in Table 5 for Run 12. The important difference between runs in which a high initial hydrogen concentration did and did not occur was the amount of steam purging of the melt that was employed prior to the start of the run. In Run 12, char from refuse pyrolyzed in the melt was gasified without any purging of the melt with steam before addition of the refuse. In Runs 8 and 9, the melt was sparged with steam for over 30 min after the char from the previous run completely reacted and before addition of the char for the subject runs.

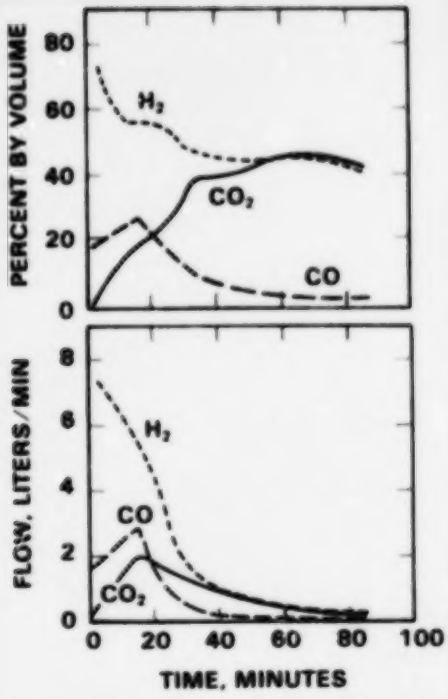


FIGURE 13. Concentration and Flow Variation with Time for Run 9

Analysis of the molten salt at the end of a char gasification run with steam as the gasifying agent showed a sodium hydroxide concentration of 33 mole %. The sodium hydroxide was apparently formed by steam decomposition of sodium carbonate as shown by the following reaction:

$$Na_2CO_3 + H_2O = 2NaOH + CO_2 \qquad (4)$$

The equilibrium constant, K, for the above reaction is the following:

$$K = \frac{X_{NaOH}^{\ 2}\, Y_{CO_2}}{X_{Na_2CO_3}\, Y_{H_2O}} \qquad (5)$$

where X_{NaOH} and $X_{Na_2CO_3}$ are the mole fractions of NaOH and Na_2CO_3, respectively, in the molten salt, and Y_{CO_2} and Y_{H_2O} are the mole fractions of CO_2 and H_2O respectively, in the vapor phase. Equation 5 assumes that the vapors behave as an ideal gas and that NaOH and Na_2O_3 have unit activity coefficients in the molten salt.

Data in the JANAF Thermochemical Tables[8] were used to compute the values of K at different temperatures. At 900°C, K has a value of 5.5×10^{-4}. Considering the melt to be composed of only NaOH and Na_2CO_3, the ratio of CO_2 to steam in the off-gas at 900°C can be calculated from Equation 5 for different mole fractions of NaOH. The rate of CO_2 evolution can then be calculated knowing the steam sparge rate, 0.23 g-mole/min in Run 9, for the case of no char present to allow competing reactions 1 and 2. At a sodium hydroxide mole fraction of 0.1, the CO_2 evolution rate is calculated to be 255 ml/min, while at a sodium hydroxide mole fraction of 0.3, the CO_2 evolution rate is only 22 ml/min. The actual CO_2 evolution rate at the end of 80 min in Run 9 when very little char is present was 200 ml/min. This indicates that Reaction 4 does influence the yields obtained when gasifying with steam.

The occurrence of Reaction 4 appears to account for the high CO_2 concentration in the gas toward the end of a run after the char is depleted by Reaction 1. Then, early in the run, the CO_2 produced by the shift reaction is absorbed by the reverse of Reaction 4, which accounts for the low CO_2 concentrations at the start of the run and high H_2 concentration. The total rate of CO_2 evolution is actually higher at the beginning of the run than at the end as shown in Figure 13, although its concentration is lower. The rate of CO_2 generation at the beginning of the run is, however, less than calculated by assuming a stoichiometric yield from Reactions 1 through 3.

The water gas shift reaction is aided early in the run by the net absorption of CO_2 by the molten salt. The overall reaction may be written as a combination of Reactions 2 and 4 as follows:

$$2NaOH + CO \rightleftharpoons Na_2CO_3 + H_2 \qquad (6)$$

The high hydrogen concentration early in the run is, then, the result of an initially high concentration of NaOH in the molten salt. Carbon dioxide produced by the shift reaction is removed from the gas stream, and in the process, water that can react with the char is released.

The occurrence of Reaction 4, or net Reaction 6, in the early stages of a run is further verified by examination of the steam decomposition at different times, listed for Run 9 in Table 6. Table 6 presents the steam decomposition based on the moles of H_2 produced compared to the moles of H_2 added in the steam with and without consideration of Reaction 6. Without consideration of Reaction 6 to determine stoichiometric yields, steam decompositions are much greater than 100% early in the

run, which is, of course, not possible. Accounting for CO_2 absorption, which releases water, and the shift reaction in determining stoichiometry reduces the steam decompositions to less than 100% at 3 min after startup. At 13 min after startup, the steam decomposition appears to be 106% even though no correction to the stoichiometric yields by consideration of Reaction 4 is required at this time. Uncertainty of the gas analysis relative to the instantaneous overall gas generation rate could account for the error in determination of H_2 generation at this time after startup, since the gas generation rate is changing appreciably at this time, as apparent in Figure 11.

TABLE 6. Steam Decomposition for Run 9

Time	Steam Decomposition, %	
	Apparent	Corrected by Reaction 4
3	131	92
13	106	106
23	63	63
33	24	24
44	15	15
59	9	9
84	5	5

Understanding of the reactions that occur in the molten salt is required for the determination of the rates of char depletion since some of the carbon compounds in the product gas could result from Reaction 4. Simply considering the carbon content in the generated gas as the amount of carbon reacted would be a serious error, since at the start of a run, a net amount of the char reacted is absorbed by the melt, whereas at the end of a run, a net amount of carbon is stripped from the melt.

The quantity of char reacted at different times during the runs on char gasification with steam was determined based on the assumption of H_2 production by the water gas and water gas shift reaction (Reactions 1 and 2 respectively) and CO_2 reaction with the NaOH in the fused salt in accordance with Reaction 3. The results obtained in steam gasification were analyzed with the assumption of stoichiometry in gas composition as a result of Reactions 1 through 4. This implies no H_2 production by further pyrolysis of the charred refuse. Calculational procedures are given in Appendix B. Equilibrium for the different reactions was not assumed in analysis of the results.

The results on gasification of char with steam were found to obey the following relationship:

$$\ln \frac{W}{W_i} = -k\theta \qquad (7)$$

where W_i is the initial weight of char in the molten salt, W is the weight of char remaining at time θ, and k is a pseudo reaction rate constant. Plots of ln(W/Wi) versus θ give a straight line with a slope of (-k), as illustrated in Figure 14. Similar relationships were noted by Kellogg in their coal gasification studies.[9] The plots in Figure 14 illustrate the linear relationship described by Equation 7. Plots such as those shown in Figure 14 were prepared for all experimental conditions to evaluate k for the different independent variables. The effect of independent variables, temperature, pressure, superficial linear velocity, and ash concentration, on the reaction rate constant k is presented in the following discussion.

The points on the plot in Figure 14 were calculated in the following manner. In the first time interval, the gas composition was determined at the end of that interval, usually 4 to 8 min after the start of the run. The entire volume of gas generated in that time interval was assumed to have the composition of the gas sample. The moles of carbon gasified were determined by considering Reactions 1, 2, and 3 to balance the H_2 and CO-CO_2-CH_4

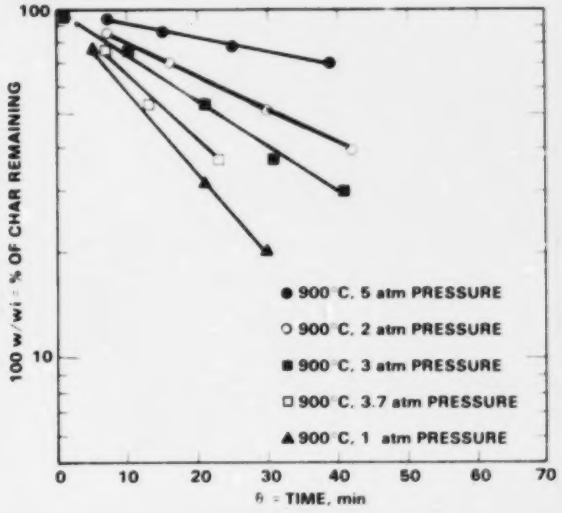


FIGURE 14. Description of Experimental Data

content. The balanced CO-CO_2-CH_4 content and the total volume were used then to determine the carbon gasified. For the following time intervals, the procedure was the same except the composition was taken as the average of the composition at the start and end of a time interval. The variation between the initial and final compositions was usually small over the time intervals of about 10 min. The time lag for initiation of reaction was adjusted by shifting the plots to force the lines to pass through 100% at time zero, a shift of about 3 min.

Values of k were determined from the slopes of plots such as those shown in Figure 14 for all the char gasification experiments. The effect of independent variables on the value of k was determined and is presented in the following discussion. The independent variables investigated for steam gasification include temperature, pressure, superficial linear velocity, and ash concentration.

Figure 15 shows the effect of superficial linear velocity on the rate constant, k, at 900°C and no initial ash content. The rate constant increases with linear velocity as expected. It would be desirable to operate at as h gh a linear velocity as expected. It would be desirable to operate at as high a linear velocity as possible to minimize the required equipment size. However, even at 0.5 fps, difficulty was experienced with crust formation in the relatively cool top regions of the reactor about 4 in. above the melt level. This difficulty could be overcome by providing heating elements in the top region of the reactor. Actual plant equipment could be designed to accommodate velocities as high as 2 fps. The superficial linear velocity is based on flow of the gasifying medium in the empty reactor cross section at reaction conditions.

The effect of ash initial content in the melt on k is shown in Figure 16 for a superficial linear velocity of 0.5 fps and a temperature of 900°C initially. The endothermic water gas reaction caused a temperature decrease of 50 to 70°C in the first 10 min of the runs. Ash content expressed as weight percent was calculated from the weight of ash in the char added to the reactor. Therefore the percent of ash does not refer to undissolved material in the melt since a portion of the ash is dissolved in the molten salt. As shown in Figure 16, the rate constant increases with increasing initial ash content. Ash in the melt has no deleterious effect on the reaction rate but must be controlled to maintain fluidity of the melt. Melts with up to 25 wt% ash could still be agitated and poured without difficulty.

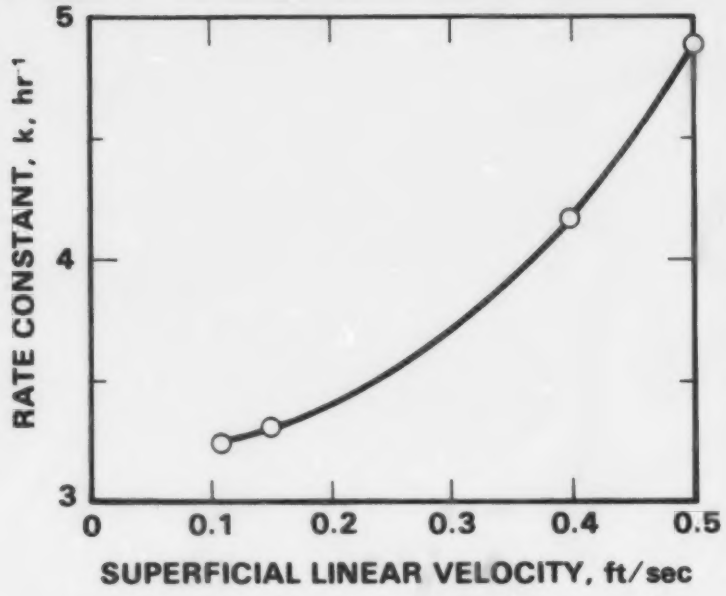


FIGURE 15. Effect of Superficial Linear Velocity on Reaction Rate Constant

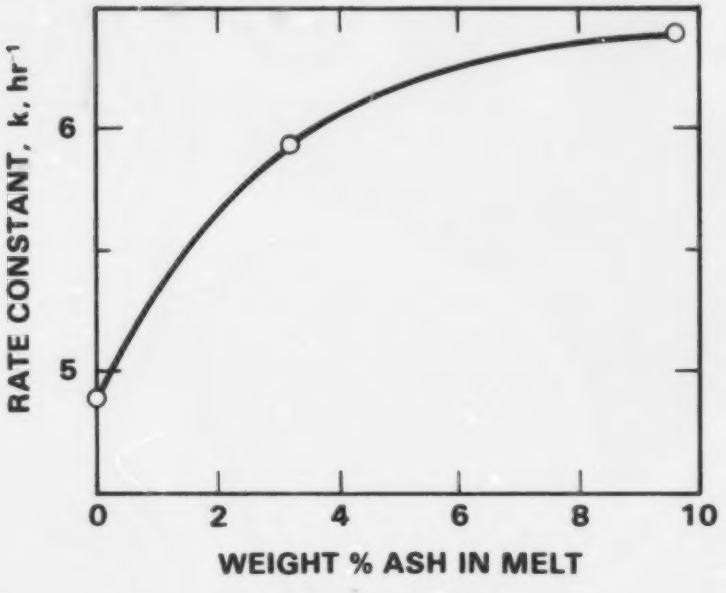


FIGURE 16. Effect of Ash Content on Reaction Rate Constant

Initial NaOH content in the melt strongly influenced the fraction of water decomposed, the amount of water reacted divided by the amount of water added. With no preconditioning to produce NaOH, maximum observed water decomposition was noted to decrease from 0.75 at 0.14 fps to 0.4 at 0.5 fps linear velocity; ash content had no observable effect on water decomposition.

The observed rate constant variation with pressure showed no definitive trend. Values of the rate constant at different pressures are shown in Table 7. It is expected that the rate constant would increase with increasing steam partial pressure; however, the rate constant decreased at pressures above 1 atm. The reason for the decrease was believed to be a result of the action of the back-pressure control valve and the steam generator. The back-pressure control valve controls the pressure in the reactor by a spring-loaded relief valve. As the flow of reaction products from the reactor increased, the pressure in the reactor was observed to increase 2 to 3 psi above the set point pressure due to a lag, or constriction in the back-pressure control valve. Steam for the reaction was provided by pumping water into a heated generator. The pump rate was constant; however, a pressure increase in the system, in effect, decreases the steam generation rate by increasing the saturation temperature for steam generation. The water level in the steam generator probably varied to compensate for the difference in steam generation rate and water delivery rate. Suspicion that steam was not delivered to the reactor at the pumping rate was further verified by the poor water decomposition calculated from the pumping rate; at 5 atm the maximum steam decomposition observed was 0.2 as calculated from the pumping rate. In summary, the anomalous results on reaction rate decrease with pressure increase are attributed to a decrease in the steam generation rate below that indicated by the water delivery rate to the steam generator. The decreased steam generation rate was a consequence of the pressure increase caused by gas generation in the reactor.

TABLE 7. Effect of Steam Pressure on Rate Constant

Superficial Linear Velocity - 0.1 fps

Initial Ash Content = 0

Steam pressure, atm	k, hr^{-1}
0.3	1.65
1	3.25
2	1.73
3	1.98
3	2.77
3.7	2.74
5	1.12
5	3.78

Runs at 3 and 5 atm pressure were repeated to try to eliminate variations in steam flow as gas generation commenced. The back-pressure valve was thoroughly cleaned prior to each run, and the steam generator was operated at pressure for over an hour to assure steady operation. The values obtained are the higher values at 3 and 5 atm shown in Table 7, but it appears the effect was not eliminated entirely.

Initial gas compositions obtained at 1, 2, 3, and 5 atm are shown in Table 8 for runs in which no preconditioning of the melt with steam to generate NaOH was used. As expected, the methane content in the gas increases with increasing pressure. No significant advantage for operation under pressure is evident for processing of municipal refuse. The data actually show a gasification rate disadvantage for operation under pressure.

TABLE 8. Initial Gas Compositions at Different Pressures

Pressure	vol%			
	H_2	CO	CO_2	CH_4
1	53.6	32.9	9.7	0.15
2	55.7	25.0	13.0	0.4
3	58.4	18.6	18.4	0.6
5	56.5	20.8	16.9	1.0

Figure 17 shows the effect of temperature on the reaction rate constant. Plots of ln k versus 1/T were not linear so an activation energy could not be calculated. The nonlinearity is probably the result of variability in char reactivity from run to run. Rates increase significantly with temperature, however, it is desirable to limit temperatures to 900°C to reduce materials corrosion problems.

Data in Table 9 show the composition of the off-gas at different times when gasifying with pure oxygen at a purge rate of 0.1 ft/sec superficial linear velocity. Complete consumption of the char is evident by the high concentration of O_2 in the final sample taken at 43 min after startup. The exothermic reaction of char with O_2 caused a 40°C temperature rise from 900 to 940°C. Operation with oxygen as the gasifying medium is technically desirable for simple operation of the gasifier. Exothermic operation of the gasifier would be easily maintained, as witnessed by the 40°C temperature rise observed in the studies, while at the same time producing a combustible gas mixture as shown in Table 9.

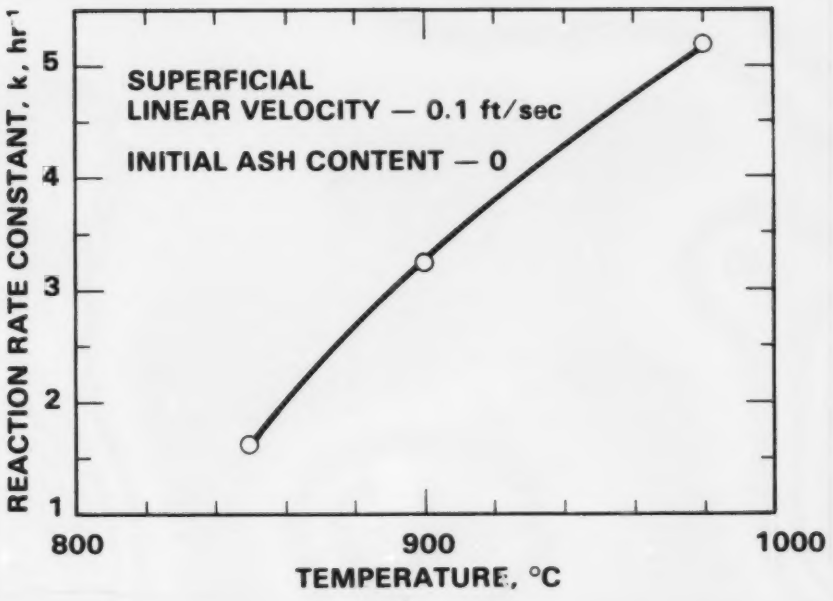


FIGURE 17. Effect of Temperature on Reaction Rate Constant

TABLE 9. Gas Compositions During Gasification with Pure Oxygen

Time after Start, min	vol% in Product Gas			
	H_2	CO	CO_2	O_2
4	5.1	88.9	4.9	<0.1
12	4.8	84.1	10.6	<0.1
24	4.7	82.4	12.6	<0.1
32	2.0	59.7	37.6	<0.1
43	0.1	3.6	52.9	41

Gasification of char with air gave no noticeable rise in salt temperature. The off-gas had about 1 vol% O_2 remaining as shown in Table 10, which shows the composition of the off-gas at different times after the start of the run. The H_2 content shown in Tables 9 and 10 results from incomplete devolatilization of the char. Reaction of char with air is exothermic, but the amount of heat generated does not exceed heat losses as in the case of operation with pure oxygen. Increasing the ratio of vessel volume to surface area will decrease the heat loss per unit volume of reactor. Exothermic reaction with air as the gasifying medium would then be possible. Operation with 4 wt% char in the melt would give the concentration shown at time 5 min in Table 10. Near stoichiometric reaction of the O_2 in air with char was observed for all superficial linear velocities investigated.

TABLE 10. Gas Compositions During Gasification With Air

Time after start, min	vol% in Product Gas			
	H_2	CO	CO_2	O_2
5	16.0	31.5	3.4	0.9
12	5.4	32.1	5.2	1.0
23	0	20.6	7.4	1.1
33	0	8.0	12.3	1.2

Results obtained in gasification of char with an O_2-steam mixture are shown in Table 11 for different times after initiation of the gasification run; no O_2 was noted in the product gas. Steam decomposition remained fairly constant as the grams of char remaining for reaction decreased. Char content at 6 min was about 3 wt%.

TABLE 11. Gas Compositions During Gasification with O_2-Steam

Time after Start, min	vol% in Product Gas				g Char Remaining	Fraction Steam Decomposition
	H_2	CO	CO_2	CH_4		
6	23.4	60.0	16.0	0.2	59.2	0.66
14	21.5	53.7	24.8	0.1	36.6	0.69
24	25.5	37.1	37.4	0.3	10.4	0.58

METHODS FOR CHARGING REFUSE

Two methods for feeding refuse to the molten salt reactor, surface feeding and submerged feeding, were investigated to determine their effect on product gas composition and product yield. Surface feeding was accomplished by simply dropping the refuse onto the surface of the molten salt and allowing the pyrolysis gas to evolve from the surface. With submerged feeding, the pyrolysis gas was forced to contact the molten salt by bubbling through it. Equipment and procedures used for the studies are described earlier. Two types of submerged feeding were used: (1) submerged feeding with salt circulation through the gas lifts to cover the charged refuse in the incineration chamber with molten salt, and (2) submerged feeding without gas lift operation (see Figure 6). Results of the runs are tabulated in Table 12. These results represent an average of at least 5 separate determinations. As expected, the gas volume generated per gram of refuse is greater for submerged feeding than for surface feeding. Intimate contact of the gases with the molten salt results in more thermal cracking of the pyrolysis products in submerged feeding than in surface feeding.

TABLE 12. Results of Feed Addition Runs

Feeding Method	Gas Volume l/g[a]	Weight Fraction Gas	Heating Value Gas, kcal/m³[a]	Heating Value Refuse/ cal/g
Submerged, gas lifts on	0.73	0.65	4000	2900
Submerged, gas lifts off	0.78	0.64	3700	2900
Surface	0.64	0.54	4800	3100

[a] Dry, N_2 free basis

As shown in Table 12, the weight fraction of refuse converted to gas is about 0.65 with submerged feeding and 0.54 with surface feeding. No significant tars and condensate were noted in the product gas with submerged feeding while 7 wt% organics and 7.5 wt% aqueous products were obtained by surface feeding. The organics had about the same viscosity as water and, therefore, were not all tarry in nature.

The total weight fraction distilled from the refuse should be the same for the two feeding methods. The agreement was nearly the same: 65 wt% of the refuse was converted to gas by submerged feeding while 68 wt% of the refuse was converted to gas and liquid products with surface feeding. It is possible that the 3 wt% difference in the two feeding methods represents a small amount of liquid product that escaped collection in the submerged feeding experiments.

The heating values in Table 12 are expressed as kcal/m^3 of product gas and as cal/g of refuse. The heating value of the refuse used in the study is given as 7203 Btu/lb (4002 cal/g) in Table 12. The heat remaining in the char is about 1100 cal/g for submerged feeding. About 70% of the refuse heating value is contained in the pyrolysis gas from submerged feeding, whereas 77% of the refuse heating value is contained in the pyrolysis gas from surface feeding. Evidently, less thermal cracking in surface feeding yields a higher heat content in the gas product. Normalized average compositions on a dry, N_2-free basis are given in Table 13 for the different feeding methods. Methane, ethane, and ethylene concentrations are significantly higher with surface feeding than with submerged feeding. This result is expected since less thermal cracking of the gas occurs with surface feeding than with submerged feeding.

TABLE 13. Composition of Pyrolysis Gas for Different Feeding Methods

Feeding Method	vol% Composition						
	H_2	CO_2	C_2H_4	C_2H_6	CH_4	CO	C_3H_8
Submerged, gas lifts on	33.6	13.6	3.4	0.5	13.4	35.5	---
Submerged, gas lifts off	40.6	11.9	1.8	0.2	11.6	33.9	---
Surface	32.4	9.9	6.5	1.0	18.3	31.8	0.05

The maximum rate for pyrolysis of refuse was based on the gas evolution rate and the heat required for pyrolysis. The heat required was calculated from the observed temperature drop upon addition of refuse and the calculated heat capacity of the molten salt reactor system. With a 6 in. depth of molten salt, the reactor system was assumed to consist of the lower 10 in. of the reactor for heat capacity calculations. The average heat requirements for pyrolysis of refuse by surface feeding was 1070 cal/g considering the salt temperature decrease and the heat capacity of the salt and the lower 10 in. of the reactor. Supplying heat for pyrolysis in a large system is possible by burning the char residue. A portion of the pyrolysis gas could also be used to supply heat autothermally.

The rate of pyrolysis was observed for both surface and submerged feeding. Up to 100 g of refuse was charged instantaneously in surface feeding with 80% of the gas evolved in the first 5 sec in the 4-in. diameter reactor. The superficial linear velocity for this case was 4.1 fps. The same situation was observed with submerged feeding, except the charge of refuse was limited to 40 g. In a large system with surface feeding, linear velocities of 5 fps should be possible.

CORROSION OF CANDIDATE CONTAINMENT MATERIALS

Since considerable information is available in the literature[10,11] no major materials evaluation study was conducted in this study. A suitable refractory containment material, Monofrax A (a high purity alumina), has been reported.[10] Metallic materials were evaluated for corrosivity and are reported below.

Studies were conducted to determine the effect of chloride on the corrosion of candidate metallic materials for use in the molten salt incinerator systems. Corrosion of Inconels 600, 601, 617, and 690, Nickel 200 and 50 Cr-50 Ni alloy was evaluated in molten sodium carbonate and in molten sodium carbonate-sodium chloride systems at 875 and 925°C and a volume-to-surface-area ratio of 150 ml/in.^{2} The alloy compositions and corrosion results are given in Tables 14 and 15.

The corrosion data indicate molten sodium carbonate is quite corrosive to all alloys investigated; and further, the corrosiveness is not altered significantly by NaCl additions up to 5 wt%. The caustic content of Na_2CO_3 melt exposed to Inconel 600 for 380 hr at 875°C was found to be about 9 wt%. Corrosion data are included for interface specimens even though about one-half of the surface of these specimens was exposed to the vapor phase and the other half to the melt. Some

preferential attack occurred at the melt-vapor interface in all cases (see Figure 18). However, this attack was appreciably greater on Inconel 690 than on the other alloys. Intergranular attack on Inconel 617 specimens was apparent, whereas attack on other alloys was largely general and uniform except for the previously noted interface attack,

TABLE 14. Nominal Composition of Test Alloys

	Wt%				
	Inc 600	Inc 601	Inc 617	Inc 690	50 Cr-50 Ni
Ni	60	72	54	60	50
Cr	23	15	22	30	50
Fe	14	8	--	10	--
Al	1	--	1	--	--
C	0.05	0.15	0.07	0.05	0.05
Mn	0.5	1	0.5	0.5	0.5
S	0.007	0.015	0.007	0.007	0.015
Si	0.25	0.5	0.25	0.25	0.25
Cu	0.25	0.5	0.25	0.25	0.25
Co	--	--	12	--	--
M	--	--	9	--	--

It is possible that Fe-Cr or low Ni-Cr alloys would exhibit better corrosion resistance to molten sodium carbonate than the subject alloys, since the system is not acting like a caustic system in its corrosion behavior. High purity alumina is reported to give good corrosion resistance in molten Na_2CO_3 systems.

Corrosion of the Inconel 600 molten salt reactor used in the gasification and pyrolysis studies was only slightly visible. The presence of sulfur was noted to cause considerable corrosion of the Inconel 600 reactor in other studies on H_2S removal that used the same equipment. No significant problems with containment were encountered in operation of the experimental equipment.

TABLE 15. Corrosion Results in Molten Sodium Carbonate and Sodium Carbonate-Sodium Chloride Systems

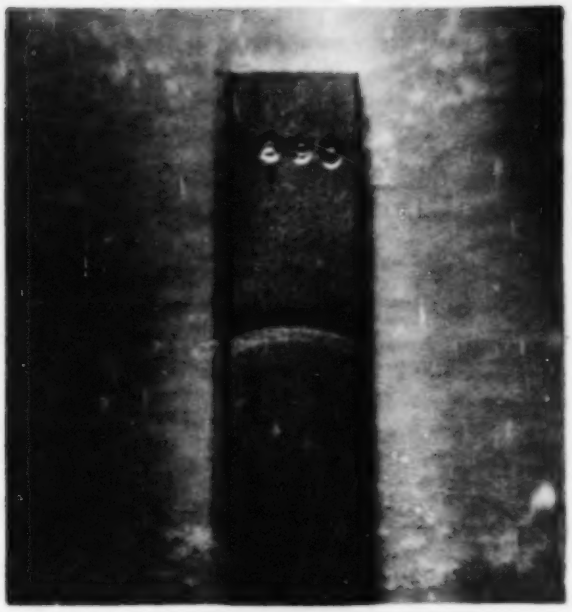
A. Molten Sodium Carbonate

	Corrosion Rate at 875°C, mpm(a)	Corrosion Rate at 925°C, mpm(a)
Inconel 600		
Melt	7.1	12.9
Interface	6.0	14.9
Inconel 601		
Melt	9.4	11.9
Interface	8.8	15.1
Inconel 617		
Melt	5.4	--
Interface	1.9	--
Inconel 690		
Melt	17.4	--
Interface	8.2	--
50_{Cr}-50_{Ni} Alloy		
Melt	5.7	--
Interface	8.9	--
Nickel 200		
Melt	Severe localized attack	--
Interface	Catastrophic	--

B. Molten Carbonate-Chloride Systems

System	Temperature, °C	Corrosion Rate, mpm			
		Inconel 600		Inconel 601	
		Melt	Interface	Melt	Interface
Na_2CO_3 - 1 w/o NaCl	875	7.2	5.8	8.5	8.0
Na_2CO_3 - 5 w/o NaCl	875	6.2	6.0	8.7	8.5
Na_2CO_3 - 1 w/o NaCl	925	13.6	12.0	13.6	9.6
Na_2CO_3 - 5 w/o NaCl	925	11.9	12.0	12.0	16.9

(a) Mils per month



INC 690

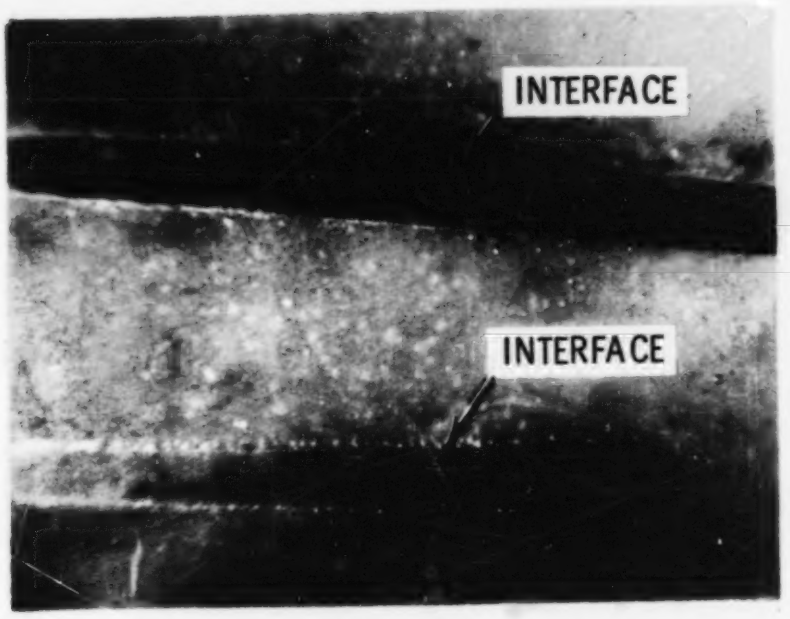


FIGURE 18 Inconel Specimens After 380 Exposure Hours to Molten Na_2CO_3 at 875°C

ASH REMOVAL

The apparatus shown in Figure 8 was used in an attempt to filter molten Na_2CO_3 containing 20 wt% ash. The entire assembly was placed in a furnace and the melt temperature was maintained at 900°C. The filter was porous stainless steel with a mean pore diameter of 5 μ; the equipment and procedures are described in the Experimental Equipment and Methods Section.

Attempts to filter the salt-ash mixture resulted in immediate plugging of the filter. Increasing the molten salt temperature to 960°C did not aid filtration. A pressure drop of 15 in. Hg across the filter was used in the filtration attempts.

Three attempts were made to filter the molten salt-ash mixture while purging with N_2 to keep the particulates suspended. The level of the molten salt-ash mixture was monitored while attempting the filtration with 1/16-in. diameter stainless steel probes which were inserted intermittently to the bottom of the molten salt container. Only one-third of the 600 g molten salt-ash mixture was removed from the container, which is about enough to fill the chamber above the filter.

Inspection of the filter after dissolving the molten salt-ash mixture in water confirmed that the filter had plugged immediately. No salt had passed through the filter. Corrosion of the filter was also noted which could have caused closure of the filter openings and blinding of the filter.

Experiments were conducted on filtration of a molten salt-ash slurry using porous alumina and porous magnesia crucibles. Filtration was effected by gravity flow through the porous walls into the crucibles which were partially immersed in the slurry. The molten salt slurry was not agitated during filtration. Ash from previous runs was added to molten Na_2CO_3 to give slurry concentrations of 5 and 15 wt% ash. The anticipated concept is the removal of molten salt through filters from a molten salt-ash slurry after the ash has settled. This would greatly reduce the amount of slurry to be generated and processed for ash removal.

Filtration of the slurry resulted in a salt which, on freezing, appeared clean with a light green color. The settled, unfiltered salt had a dirty appearance and was light brown in color.

Results of the analysis of filtered and unfiltered salt are shown in Tables 16 and 17 for filtration of a 5 and 15 wt% slurry, respectively. The amount of Al and Si in the molten salt was surprisingly low; the Al and Si contents in other experiments were each about 0.2 wt%. Typical ash composition obtained in

previous runs in shown in Table 18. Apparently, the particular ash used for this study either had very little Al and Si or, for some reason, these components did not redissolve. From these data, the only cleanup obtained by filtration was some removal of the iron. Filtration through magnesia resulted in slight dissolution of Mg. Simple settling was quite satisfactory for salt cleanup, as apparent in Tables 16 and 17.

TABLE 16. Results on Filtration of a 5 wt% Slurry

Component	Concentration in Supernate		
	After Settling	Filtered Through Porous Alumina	Filtered Through Porous Magnesia
Al	25 ppm	25 ppm	25 ppm
Ca	0.2 wt%	0.22 wt%	0.61 wt%
Mg	125 ppm	125 ppm	500 ppm
Si	<0.01 wt%	0.01 wt%	0.01 wt%
Fe	375 ppm	300 ppm	250 ppm

TABLE 17. Results on Filtration of a 15 wt% Slurry

Component	Concentration in Supernate	
	After Settling	After Filtration Through Porous Alumina
Al	25 ppm	25 ppm
Ca	0.94 wt%	0.59 wt%
Mg	250 ppm	125 ppm
Si	<0.01 wt%	<0.01 wt%
Fe	1625 ppm	149 ppm

TABLE 18. Typical Metal Concentrations in Ash

Component	Concentration, wt%
Al	4.4
Ca	7.5
Si	2.8
Fe	8.0

Cleanup by simple settling was not as effective as noted in Tables 17 and 18 when the ash was generated in the melt during gasification of char. Salt samples were taken from a melt with

8.8 wt% ash after the melt was left quiescent for a sufficient time to allow settling of the particulates. The ash was operated during char gasification studies. The samples were analyzed for Na, Fe, Si, and Al dissolved in the melt. Concentrations of these components in the ash and salt are shown in Table 19.

TABLE 19. Concentration of Al, Fe, Si, and Na in Ash and Melt

	Wt%			
Substance	Al	Fe	Si	Na
Ash	4.2	4.8	8.62	5.2
Molten Salt	0.22	0.18	0.66	45

Concentrations in the molten salt represent the amount of dissolution of these elements. The amounts of dissolved elements compared with the total amounts recovered in the ash show that 59% of the Al, 43% of the Fe, and 87% of the Si in the ash are dissolved in the molten salt.

Concentration of the ash in the molten salt by settling is possible. Samples of the molten salt-ash slurries show a definite gradient in ash concentration from the top to the bottom in a quiescent melt. The tops were found to contain 0.74% water insoluble ash while the bottoms contained 7.4% water insoluble ash.

Ash from the gasification runs was recovered by dissolution of the salt cake in water at the end of a run sequence. Table 20 summarizes the recovery of ash from the melt. The ash after drying is an extremely fine powdery material that dusts very readily. The percent recovery in Table 20 is based on the amount of ash expected in the salt as determined by the ash content in the char added to the salt. The ash losses resulted from some evident losses in filtrate. The recovery of over 100% of the ash represents incomplete washing of the salt from the ash. It should be noted that the amount of ash in the char does vary such that the amount of ash charged to the molten salt with the char is not known precisely.

TABLE 20. Ash Recovery by Dissolution in Water

Runs	Weight Melt, g	Weight Ash Recovered, g	% Recovery
2,3,4	2,500	110	92
5,6,7	2,500	143	93
8,9,10,11,12	2,500	212	95
13,14	2,500	102	75
18,19,20	2,500	204	108

The ash residue in the aqueous solution had the filtration characteristics of a crystalline precipitate. Filtration of the ash obtained by dissolving the ash-laden salt was easily accomplished.

Recovery of aluminum from the molten salt by tapping molten alumina from the reactor was envisioned as a possible advantage of the process. Attempts to demonstrate this were unsuccessful. The aluminum was oxidized in the melt.

CONCEPTUAL PLANT AND ECONOMICS

Engineering flow diagrams, a conceptual plant design, and economics for a 200 tons/day and a 1000 tons/day pilot plant were developed. The flow diagrams, plant design, and economics were based on the research conducted during this program and work conducted by The M. W. Kellogg Company for the United States Department of Interior's Office of Coal Research.[10,12]

ENGINEERING FLOW DIAGRAM

Results obtained in the experimental studies were used for development of the flow diagram required for preliminary estimation of the economics of molten salt processing of municipal refuse. It was assumed that the most attractive economics would be obtained by use of air to combust a portion of the carbonaceous material for generation of the heat required for the process, rather than using oxygen or oxygen-steam mixtures, since an oxygen plant is very costly. Because typical municipal refuse has a small fraction (only about 20 wt%) of char, use of steam for char gasification was determined to be impractical since combustion of over 90% of the char to CO and CO_2 was required to generate the energy required to sustain an autothermal process.

The conceptual flow sheet for operation with a two compartment reactor is shown in Figure 19, while material and energy contents of the numbered stream is shown in Table 21. Mass balance calculations are given in Appendix C.

Combustion of the char to produce heat is accomplished in one compartment, and pyrolysis and drying of the refuse is accomplished in a second compartment. In this mode of operation, a pyrolysis gas of composition shown in Table 13 for surface feeding is obtained.

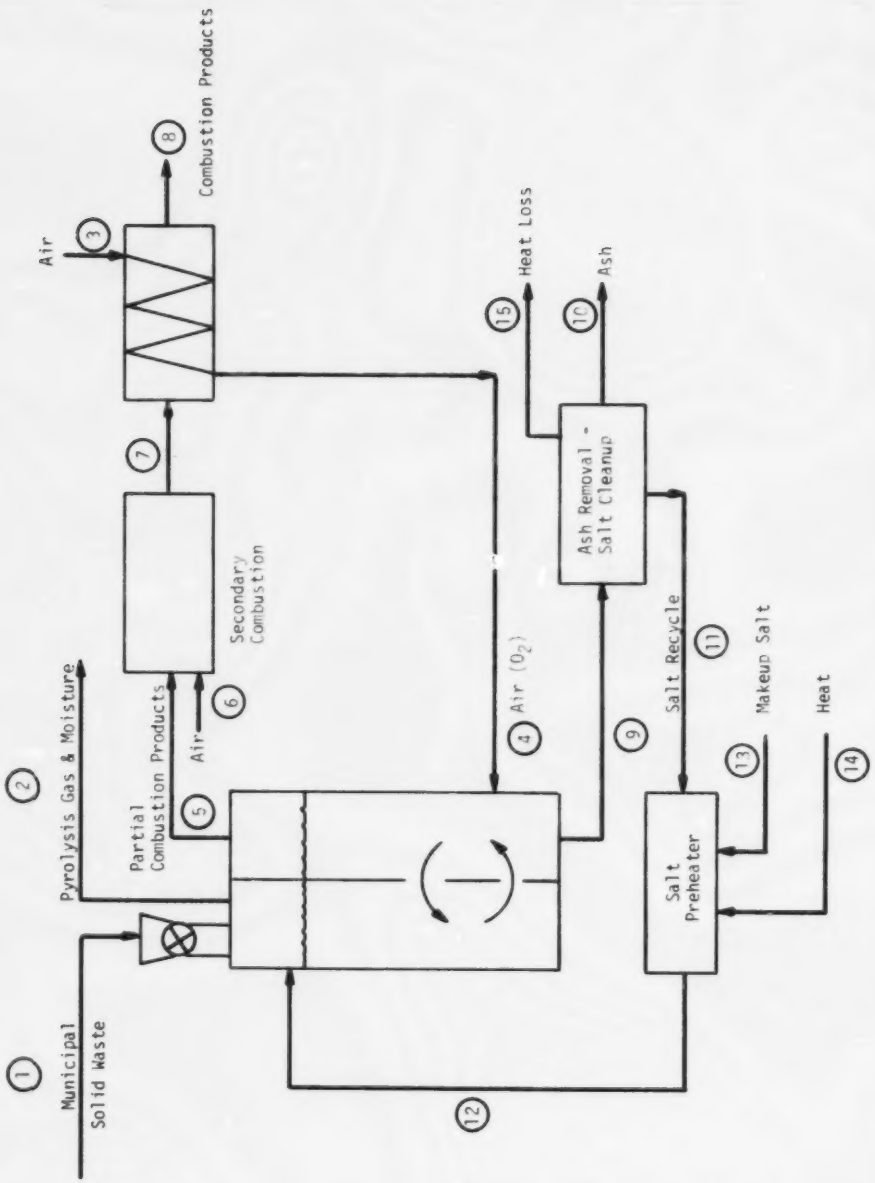


FIGURE 19. Flow Diagram for Molten Salt Pyrolysis Combustion Process

TABLE 21. Mass and Energy Values for Streams Shown in Figure 19

Stream No.	Mass Flow	Volume Flow, scfm	Energy Flow Btu/hr	T, °C	P, psig
1	1800 tons/day	3400	80.3×10^6	470	
2		4420	68.9×10^6	25	10
3					
4		4420	7.0×10^6	700	10
5		4640	17.1×10^6	700	3
6		1330	0	25	3
7		5490	17.1×10^6	1260	3
8		5490	10.1×10^6	750	2
9	75.3 tons/day	44 ft^3/hr	3.7×10^6	900	
10	21.1 tons/day		0	25	
11	54.3 tons/day		0	25	
12	56.5 tons/day		2.7×10^6	900	
13	2.2 tons/day		0	25	
14			2.7×10^6		
15			3.7×10^6		

For calculation, the gas composition from the combustion chamber was taken to be about the same as the value shown in Table 10 at time 33 min, 10% CO, 15% CO_2, and 75% N_2.

The flowsheet is based on 200 tons/day municipal refuse that contains 10 wt% bulk and ferrous metals. The feed to the molten salt reactor, 180 tons/day, was assumed to contain 30 wt% water and have the ultimate and proximate analyses shown in Table 2. The ultimate and proximate analyses adjusted to 30 wt% water are shown in Table 22.

TABLE 22. Ultimate and Proximate Analysis of Refuse Used in Flowsheet Development

Proximate Analysis	wt%
Moisture	30
Volatile at 950°C	59.5
Ash	10.5
Calorific value 5100 Btu/lb	
Ultimate Analysis	
Moisture	30
Carbon	34
Hydrogen	5.2
Oxygen	21.2
Nitrogen	3.1
Sulfur	0.1
Chlorine	0.2
Ash	10.5
CO_2	10.5

The heat required in the salt preheater must be obtained from combustion of a portion of the pyrolysis gas. The potential heat content in stream 2, the pyrolysis gas, is 61.3×10^6 Btu/hr. The heat required for salt preheat is 2.7×10^6 Btu/hr, which gives a net potential heat of 58.6×10^6 Btu/hr. The cold gas efficiency of the process is thus seen to be $\frac{58.6 \times 10^6}{80.3 \times 10^6} \times 100 = 73\%$.

The total heat going into the molten salt reactor is the sum of streams 1, 4 and 12 which totals 90×10^6 Btu/hr. The heat coming out, streams 2, 5, and 9, is slightly less at 89.7×10^6 Btu/hr. This allows for a 0.3% heat loss for the process to be autothermal. It was assumed that greater heat losses could be compensated by use of a small fraction of the product gas.

Single compartment operation was assumed to be identical to operation with a two-compartment system as far as material and energy flows are concerned. Inlet streams are identical and outlet streams are the same except the outlet gases are combined into a single stream which is the sum of streams 2 and 5 as shown

in Figure 19. Thus, the total flow rate is 8040 scfm for the single compartment product gas and the composition is that shown in Table 23.

TABLE 23. Single Compartment Product Gas Composition

Component	H_2	CO_2	C_2H_4	C_2H_6	CH_4	N_2	CO	H_2O
Vol%	6.1	11.0	1.5	0.2	4.3	44.9	13.2	18.8

The combustion compartment was sized assuming a 2 fps superficial linear velocity. The cross-sectional area required for the combustion section was calculated to be 158 ft^2. Surface feeding was assumed for the pyrolysis section, and a 5 fps superficial linear velocity was assumed tolerable; the calculated area required was 36 ft^2. The single vessel system has the advantage that the vessel cross-sectional area is the same as for the combustion compartment in the two compartment reactor, which is 158 ft^2. A shallow depth is tolerable for the reactor and was taken to be 15 ft.

The product gases were found to be free of oils and tars in the experimental studies and no cleanup of the gases should be required for use as a boiler feed. A heat exchange with a transfer area of 250 ft^2 was required to preheat the air to the process.

PLANT DESCRIPTION

The conceptual design for a molten salt pyrolysis plant that would be capable of receiving municipal, commercial, and industrial solid waste and conversion of the solid waste to a low Btu gas was developed. The flow diagrams that are described in the previous section were used as the basis for determining the size of the equipment required for the plant. The facility will consist of a solid waste receiving and feed preparation complex, a molten salt gasification, ash removal and handling, salt preparation and handling, and gas handling complex, as well as support facilities. A schematic of the equipment flow diagram is shown in Figure 20.

The solid waste receiving and feed preparation complex is similar to the feed preparation systems for most of the resource recovery systems being developed. Solid waste is received in a covered area equipped with receiving hoppers that will accept waste from incoming vehicles. The storage capacity of the system prior to the shredder would be equal to the 24-hr capacity of the plant. The vehicles would be

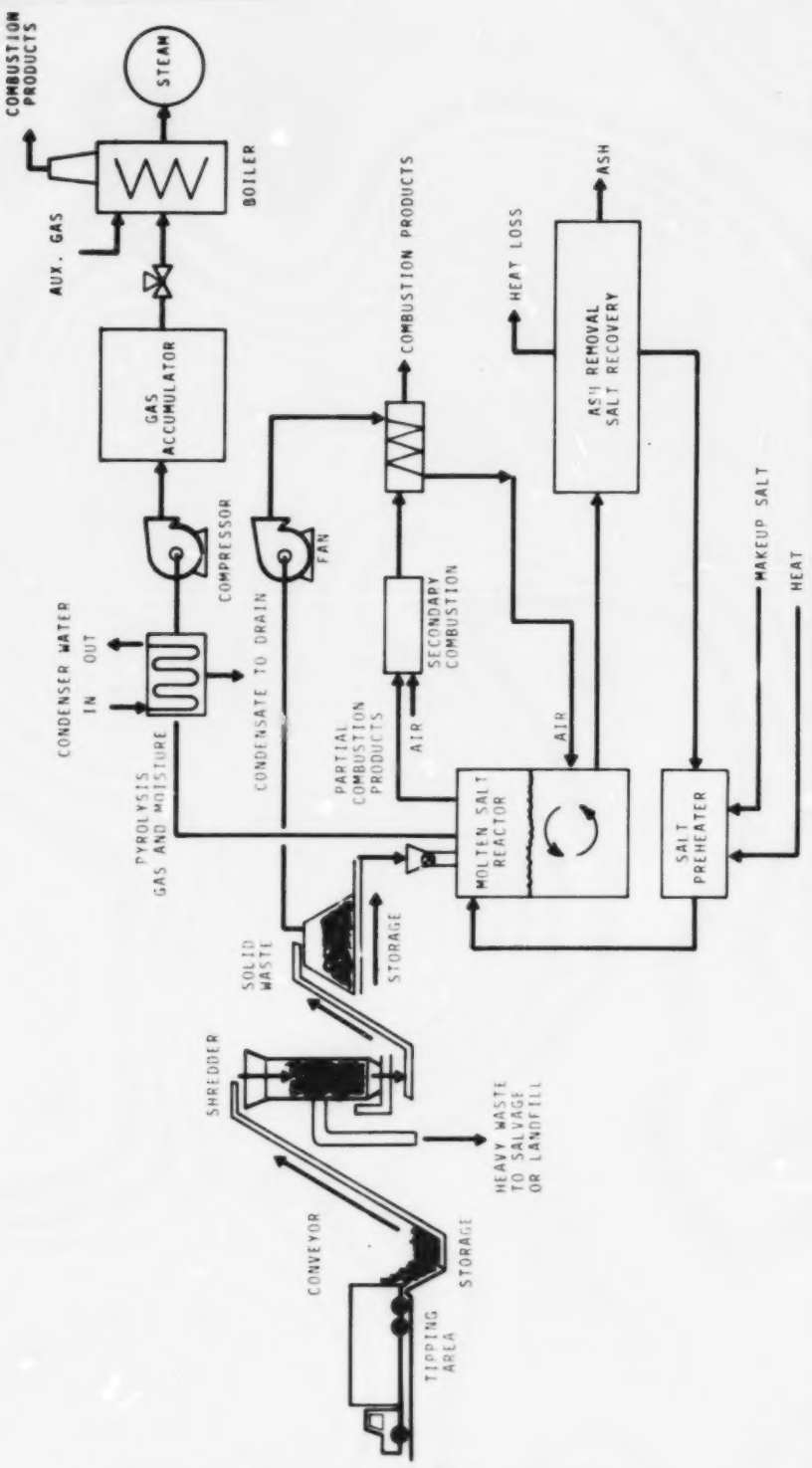


FIGURE 20. Equipment Flow Diagram

weighed on entrance to and exit from the facility to insure an accurate accounting of the waste that is processed in the facility. The solid waste will be conveyed from the receiving area to the shredder by belt conveyors. The feed rate of the conveyors will be automatically controlled to insure that the shredder is not overloaded. The hammer mill type shredders will be sized to handle the 24-hr plant capacity in a maximum 16 hr to allow for maintenance on the shredder. A minimum of 8 hr storage capacity is required between the shredder and the gasifier.

The wastes will be conveyed from the shredder to the storage bin by a belt conveyor equipped with a magnetic separator for removal of ferrous materials from the feed stream. Live bottom storage bins will be required between the shredder and the gasifier to insure that the solid waste can be fed to the gasifier at a uniform rate. Belt conveyors will be used to move the solid waste from the storage bins to the gasification system.

The solid waste will be fed by a screw feeder or a plunger type feeder into the molten salt pyrolysis-gasification reactor. The reactor and all piping to and from the reactor will have to be lined with Monofrax A, which is a high purity fused cast alumina. Corrosion studies[10] indicated that this is the only material that will withstand the process for any length of time. Further work is required in this area to identify other potential materials of construction, since the use of Monofrax A lined vessels and piping makes the capital cost of the process equipment extremely high. A 15-ft O.D. x 28-ft high reactor vessel with an 8-in. thick Monofrax lining is required for a 200 tons/day facility. Two 11-ft O.D. x 22-ft high vessels could also be used for the 200 tons/day facility. Manufacturing and transportation constraints will dictate the maximum vessel size to be used in a 200 tons/day facility since the cost of a single or double reactor facility is almost identical.

The two feasible alternatives for disposal of ash are removal of ash from the salt and disposal of ash and the salt together; both alternatives have about the same cost. Since disposal of the ash and salt together has the possibility of creating environmental problems, the salt removal and cleanup route was selected as the best alternative. The salt removal and cleanup process will be similar to the one used in the Kellogg coal gasification process. The ash will be stored in hoppers for removal to a sanitary landfill or for use as industrial fill. The slip stream of ash and molten salt will pass through a quench tank for cooling, a grinder for size reduction, a tank

to put the salt in solution, an ash filter for solids removal and a carbonation tower to regenerate the salt. Then the salt will be filtered from the slurry stream and dried before being recycled back to the molten salt gasifier. Equipment for the ash removal and salt preparation process is described in the Office of Coal Research reports on the Kellogg coal gasification process.[10]

The pyrolysis gases and moisture are passed through a condenser to remove all water and other condensate prior to being compressed and fed into the gas accumulator. In cases where all the gas can be burned immediately, the condenser, compressor, and accumulator can be replaced with a low pressure fan. The gas handling system is heavily dependent on the type of system in which the low Btu gas will be used. For the conceptual design and cost estimating, it was assumed that a minimum of two buildings would be required, one for the solid waste receiving and feed preparation equipment, and the second one to house the gasification, salt handling, and ash removal equipment.

ECONOMICS OF MOLTEN SALT PYROLYSIS-INCINERATION PROCESS

The capital costs, operating costs, and potential revenue were developed for facilities capable of handling 200 and 100 tons/day of solid waste. The economics developed for these facilities are based on past experience in similar programs such as the Pyrolysis-Incineration Process for Solid Waste Disposal,[13] Office of Coal Research's work on the Kellogg process,[10] and Popper's Modern Cost Engineering Techniques.[14] The economics for solid waste processing facilities using molten salt technology show the processes to be capital sensitive and not economically competitive with other waste conversion processes that produce energy as the main revenue producing product. Factors other than economics would be required to make the process attractive as a method of handling solid waste.

The capital costs for 200 and 1000 tons/day are shown in Table 24. These costs are for a facility producing gas that can be fed into a steam boiler and includes the gas cleanup system as well as the accumulator. However, none of the costs of boiler modification were included and the cost of land is not included in the capital cost estimate, which range from a high of $60,700 to a low of $43,800/ton of waste processing capacity per day.

TABLE 24. Capital Cost Estimate for Solid Waste Molten Salt Gasification Facilities

Item	200 tons/day Facility	1000 tons/day Facility
Feed Preparation System	$ 800,000	$ 3,100,000
Gasification System	7,000,000	25,000,000
Support Facilities	290,000	1,100,000
Subtotal	8,090,000	29,200,000
Engineering at 20% of Subtotal	1,620,000	5,800,000
Contingencies at 30% of Subtotal	2,430,000	8,800,000
Total Capital Cost	$12,140,000	$ 43,800,000
Capital Cost, $/tons/day	$60,700	43,800

A scale-up factor on the order of 0.8 can be used for capacities of from 200 to 1000 tons/day. For larger facilities, the scaleup factor will approach 1 and costs will be directly proportional to capacity. The total capital cost could be reduced to about one-half of the costs shown in Table 24 if the material and fabrication costs of the gasification processing equipment were similar to those for stainless vessels and piping. The probability of reducing the capital costs to one-half of the capital costs shown in Table 24 is about 10%.

Operating costs and potential revenue are shown in Table 25. Those costs, associated with the capital cost of the facility, are in excess of 50% of the total operating cost which makes the operating cost of the facility capital sensitive.

The average plant life for this facility was assumed to be 15 years. The rationale for this assumption is that the major capital costs are associated with the gasification equipment and that, with respect to the present state-of-the-art and no long term operating experience, the plant could not be expected to last more than 15 years without major capital expenditures. This assumption seems valid even though the building and a large portion of the installed equipment may not need to be replaced for up to 40 years. The 6% interest was selected as a nominal rate and would vary according to the type of organization responsible for the facility and interest rates at time of construction.

TABLE 25. Economics of Solid Waste Molten Salt Gasification Facilities

Item	200 tons/day Facility	1000 tons/day Facility
Amortization and Interest at 6%, 15 year plant life	$1,250,000	$4,510,000
Maintenance at 5% of Capital Cost	610,000	2,190,000
Operating Labor and Supervision	338,000	574,000
Overhead at 90% of Labor	304,000	400,000
Sodium Carbonate Make-up at $0.015/lb	30,000	150,000
Power at 5 mills per kW-hr	50,000	250,000
Chemicals and Supplies	50,000	200,000
Taxes and Insurance at 2.5% of Capital Cost	305,000	1,095,000
Total Annual Operating Cost	$2,937,000	$9,369,000
Operating Cost for a Facility Using Air as the Process Oxidant, $/ton	$40.23	$25.66
Oxygen Cost at 1/4 ton of Oxygen per ton of Solid Waste	$ 5.50	$ 2.50
Operating Cost for a Facility Using Oxygen as the Process Oxidant, $/ton	$45.73	$28.16
Revenue from Low Btu Gas at $1/$10^6$ Btu, $/ton Solid Waste	$ 7.03	$ 7.03
Disposal Cost for a Facility Using Air as the Process Oxidant, $/ton	$33.20	$18.63
Disposal Cost for a Facility Using Oxygen as the Process Oxidant, $/ton	$38.70	$21.13

The operating cost of $40.23/ton for 200 tons/day, $25.66/ton for 1000 tons/day facilities as shown in Table 25 are at least twice the operating costs that would be associated with other pyrolysis or incineration facilities of comparable size. No economic incentive was identified for using oxygen in the process instead of air if the low Btu gas is used as an industrial heating gas or used for the production of steam.

The operating costs could be reduced to $27.00/ton and $15.00/ton for 200 tons/day and 1000 tons/day plants, respectively, if the capital costs could be reduced to one-half the costs shown in

Table 24. Several years of materials research, plant development and optimization would be required to bring the capital and operating costs to this lower level.

The potential revenue from this process will depend on the price of alternate fuels in the area where the plant is being constructed. The utilities price for fuels, as reported in "Electrical Week", March 26, 1973, ranged from a low of $\$0.17/10^6$ Btu to a high of $\$2.52/10^6$ Btu.[15] The price of fuel for power plants and industrial uses is a function of the:

- Type of purchase (contract, spot, firm, or interruptible).
- Type of control on price (intrastate or interstate fuel).
- Type of fuel (coal, gas, or oil).
- Amount of sulfur in the fuel.
- Origin of the fuel and amount of transportation required.
- Supplier (self-supplied or purchased).

The spot price for No. 2 and No. 6 fuel oil as reported in the August 27, 1973, Electrical Week ranged from \$0.848 to \$1.397 and \$0.72.3 to \$1.117 per 10^6 Btu, respectively.[16]

Since a very limited amount of natural gas is available for new contracts, it appears that the only available fuel for industrial heating or steam production that is available for new applications is either coal or oil. Since the low Btu fuel is a clean fuel, No. 2 fuel oil prices provide a good data base for determining the price that could be charged for low Btu gas. The present data indicate that the price for future contracts and spot sales of low sulfur No. 2 fuel oil will be in excess of $\$1.00/10^6$ Btu, which justifies using $\$1.00/10^6$ Btu for the sale price of the gas generated by this process. Future supplies of synthetic gas produced from coal are estimated to be in the range of \$1.00 to $\$1.50/10^6$ Btu. It should also be noted that the prices for fuels are changing very rapidly and past trends may not be a good indication of future fuel prices, but for the next 10 to 20 years all indicators point to higher prices. In summary, it appears that $\$1.00/10^6$ Btu will be a minimum price for new supplies of clean fuel.

The price of $\$1.00/10^6$ Btu was used in the revenue calculations shown in Table 25. The process will produce 7.03×10^6 Btu of

salable gas for every ton of received solid waste that is processed. This will provide a revenue of about $7.03/ton of solid waste on the basis of $1.00/$10^6$ Btu. Other pyrolysis processes are estimated to produce up to 7×10^6 Btu/ton of solid waste. In order for this process to be competitive with other resource recovery processes, the cost of producing energy by this process will have to be reduced, because the other processes are estimated equally or more efficient in the production of energy while the operating costs for energy production are less.

Labor distribution for the operation of a molten salt pyrolysis facility is shown in Table 26. Adjustments to this labor distribution will depend on the type of organization operating the plant. The primary assumption for this distribution was that the facility was to be operated by a city that did not have this type of operation. If the facility was operated by a city or utility that also had responsibility for operation of a power plant or district heating system that would utilize the power, the cost of labor could be reduced by up to 10%. Since the operating costs are capital sensitive rather than labor sensitive, a 10% reduction in labor costs would reduce the total operating costs by 2.2%. Highly trained people are required to operate a molten salt pyrolysis facility, compared to most other resource recovery systems, due to the complexity of the process and the hazards associated with operation of a molten salt facility.

TABLE 26. Plant Labor Distribution

Description	Wage	200 tons/day Facility		1000 tons/day Facility	
		Number	Payroll	Number	Payroll
Plant Manager	$25,000	1	$25,000	1	$25,000
Secretary	8,000	1	8,000	1	8,000
Plant Engineer	20,000	1	20,000	2	[illegible]000
Shift Supervisor	15,000	4	60,000	6	9[illegible]00
Clerks	6,000	1	6,000	2	12,[illegible]
Process Operators	12,000	12	144,000	24	288,000
Weigh Master	7,500	1	7,500	1	7,500
Traffic Director	7,500	1	7,500	1	7,500
Plant Maintenance	12,000	4	48,000	6	72,000
Labor Cleanup	6,000	2	12,000	4	24,000
TOTALS	$119,000	28	$338,000	48	$574,000

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APPENDIX A

ANALYTICAL PROCEDURES FOR OFF-GAS ANALYSIS

ANALYTICAL PROCEDURES FOR OFF-GAS ANALYSIS

Gas analysis for charred and uncharred garbage in molten salt was obtained using the equipment and equipment conditions as described below.

EQUIPMENT

A Hewlett-Packard model 7624A gas chromatograph was used for gas analysis with the off-gas samples being taken from the sample stream after passing through a flow meter to measure total volume through the sample system and a drierite column to remove moisture from the sample (Figure A-1). Approximately 1.0 to 1.5 liters of sample volume was passed through the sample system before valving a gas sample onto the columns. A heated gas sampling valve equipped with 0.5 cm^3 sample loops injected the sample onto the columns.

The off-gas composition was such that obtaining complete resolution of all components on a single column in a reasonable length of time was difficult. Therefore, the dual-columns-in-series arrangement described below and shown schematically in Figure A-2 was adopted.

The components of the product gas were completely separated on two columns in series, with a switching valve between the columns to allow the second column to be bypassed. The first column in the series was a 10 ft x 1/8 in. SS Porapak Q[a] (50-80 mesh) and the second column was a 10 ft x 1/8 in. Molecular Sieve 5A[b] (60-80 mesh). The switching valve allowed the CO_2, ethane, ethylene, propane and higher boiling compounds to be eluted directly from the Porapak column to the detector, thus bypassing the molecular sieve column required for good separation of oxygen and nitrogen.

The carrier gas used has a composition of 8.5% H_2 and 91.5% He. This mixture increased the sensitivity to H_2 by a factor of two over what could be obtained with pure He as the carrier gas. A Carle model 8000 gas chromatograph with an 8 ft x 1/8 in. Carbosieve[c] column was also used as a back-up for H_2 analysis; N_2 was used as a carrier gas and the column was unheated for elution of H_2.

(a) Trademark, Waters Corporation
(b) Trademark, Linde Corporation
(c) Trademark, Supelco Corporation

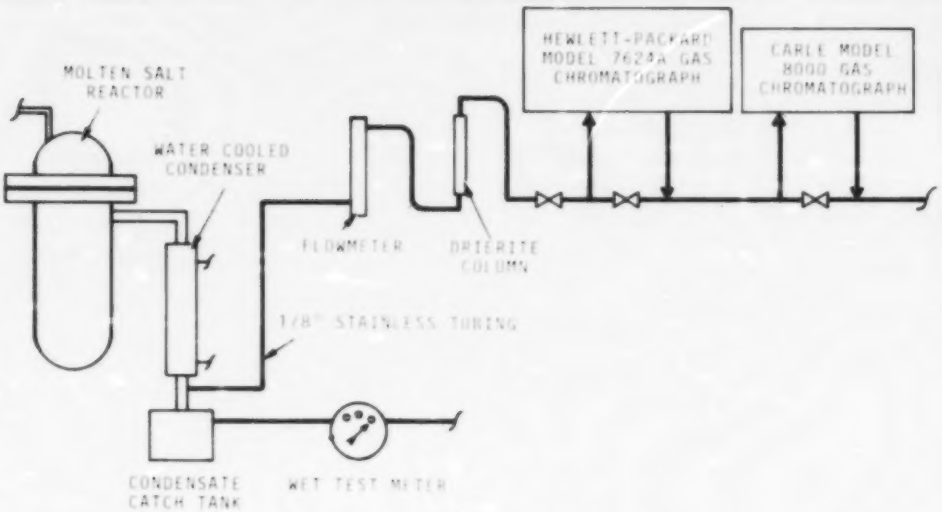
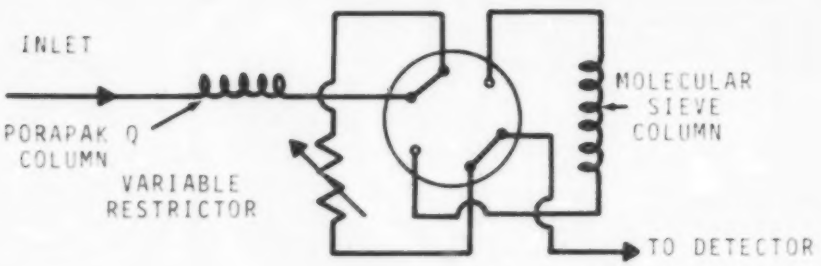
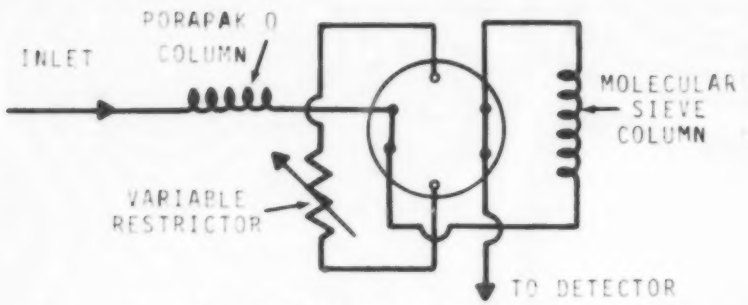


FIGURE A-1. Char Reactor Off-Gas Sampling Train



a. VALVE IN BYPASS MOLECULAR SIEVE COLUMN POSITION



b. COLUMNS IN SERIES POSITION

FIGURE A-2. Schematic of Gas Chromatograph Column Switching Valve

The calibration curves were prepared using analytically certified gas mixtures prepared by the Matheson Company. All peak areas were integrated by a Hewlett-Packard Model 3370 electronic integrator except the H_2 obtained from the Carle gas chromatograph which was calibrated by measuring peak height.

EQUIPMENT CONDITIONS

Hewlett-Packard Gas Chromatograph Conditions for Analysis of Charred Municipal Refuse in Molten Salt

- Sample Valve Temperature - 150°C
- Detector Temperature - 150°C
- Bridge Current - 175 ma
- Oven Temperature - 60°C to 215°C at 30°C/min rate with 1 min hold times at 60, 80 and 215°C
- Carrier Gas - Helium with 8.5% Hydrogen mixture at 50 cc/min flow
- Column switching and elution order:

  1. The sample was injected into the Porapak Q column with the columns connected in series.
  2. H_2 was eluted after 2 min.
  3. When O_2, N_2, CH_4, and Co had eluted onto the molecular sieve column, the valve was switched to bypass the molecular sieve column and elute CO_2 from the Porapak column directly to the detector. (These compounds would have been permanently absorbed if allowed to pass onto the Molecular Sieve column.)
  4. After elution of CO_2, the valve was switched back to connect the columns in series and O_2, N_2, CH_4, and CO were eluted from the Molecular Sieve column in that order.

Hewlett-Packard Gas Chromatograph Conditions for Analysis of Uncharred Garbage in Molten Salt

- Sample Valve Temperature - 150°C
- Detector Temperature - 150°C

- Bridge Current - 175 ma
- Oven temperature - 60°C at 215°C at 30°C/min with a 1 min hold time at 60°C, 4 min hold time at 80°C, 2 min hold time at 120°C, and 4 min hold time at 215°C.
- Carrier Gas - Helium with 8.5% H_2 mixture at 50 cc/min flow
- Column switching and elution order:

  1. The sample was injected onto the Porapak Q column with the columns connected in series.
  2. H_2 was eluted after 2 min.
  3. When O_2, N_2, CH_4 and CO had eluted onto the molecular sieve column, the valve was switched to bypass the molecular sieve column and elute CO_2, ethane and ethylene from the Porapak column directly to the detector. (These components would have been permanently absorbed if allowed to pass onto the Molecular Sieve column.)
  4. After elution of ethane, the valve was switched back to connect the columns in series and O_2, N_2, CH_4 and CO were eluted from the Molecular Sieve column in that order.
  5. The valve was again switched to the bypass position and propane and traces of other unidentified high boiling compounds were eluted directly from the Porapak column to the detector.

Typical chromatograms are shown in Figure A-3 for charred garbage and Figure A-4 for uncharred garbage.

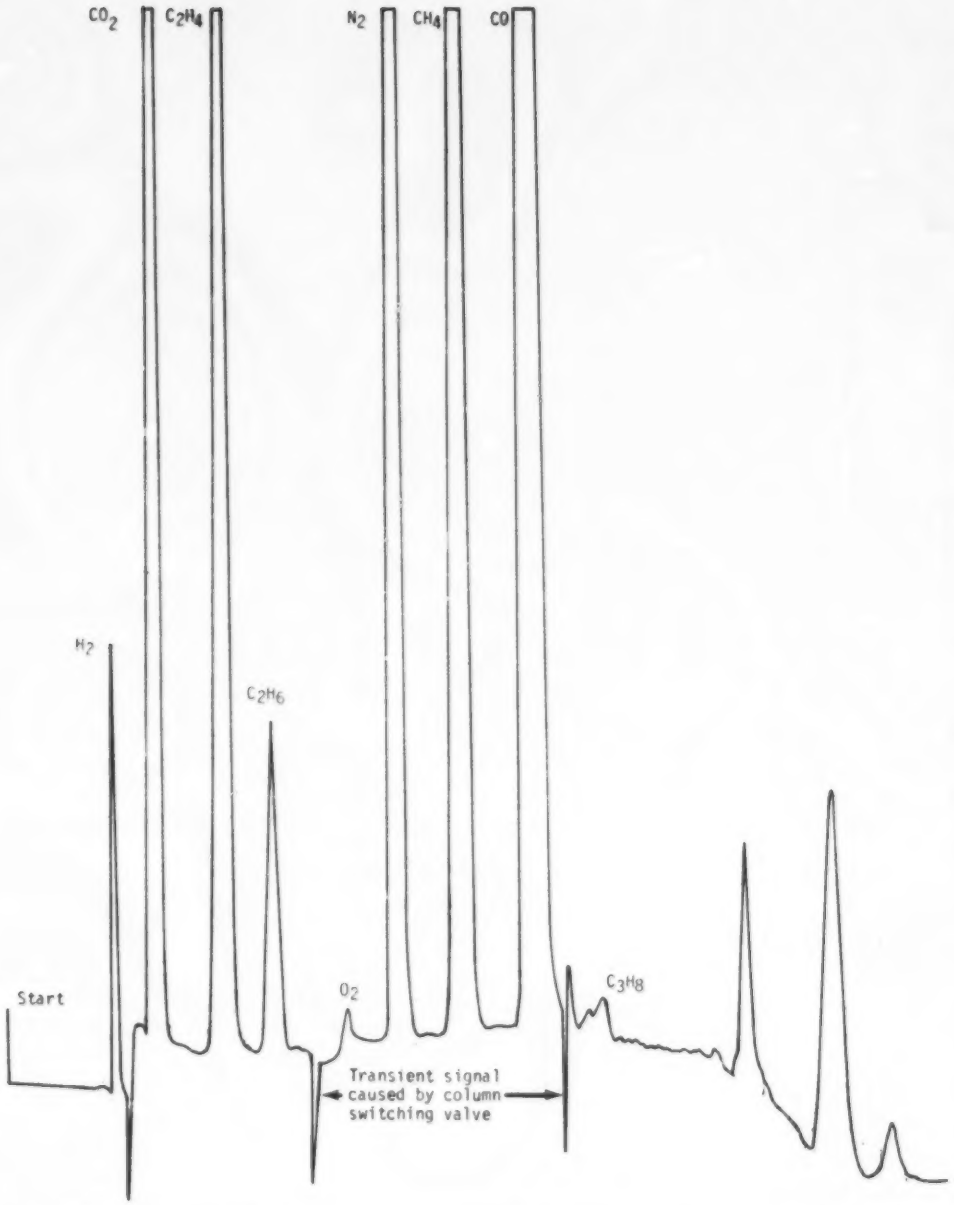


FIGURE A-3. Sample Chromatogram for Analysis of Pyrolysis Products

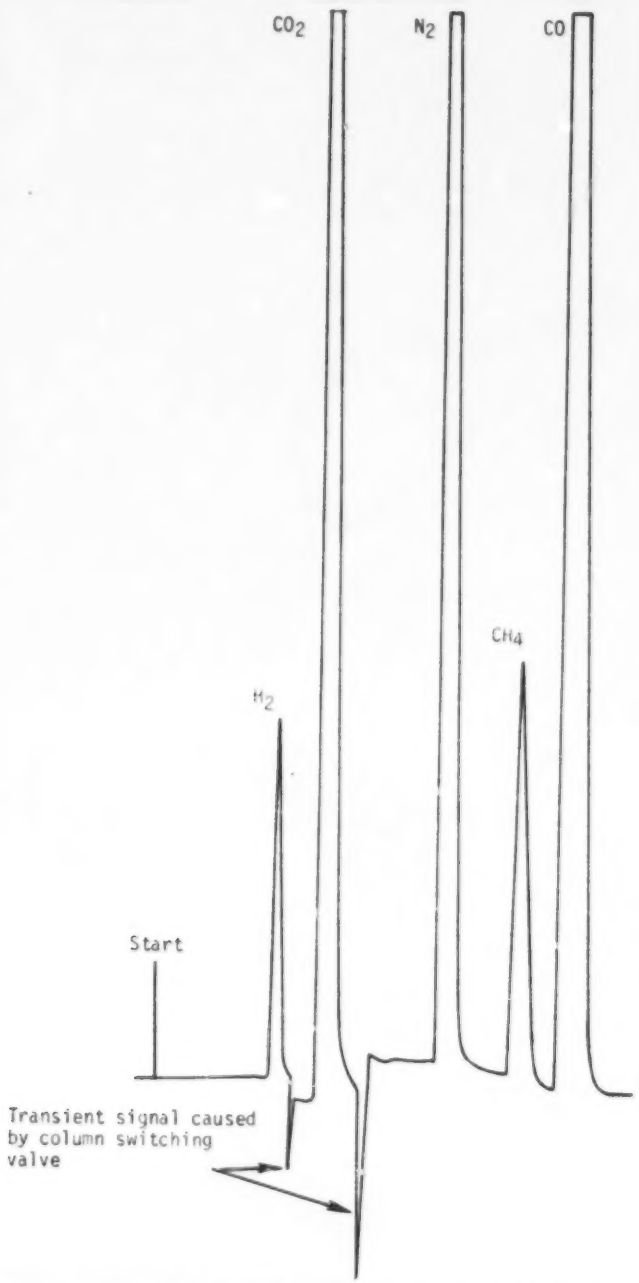


FIGURE A-4. Sample Chromatogram for Analysis of Products from Char Gasification

APPENDIX B

METHOD FOR CALCULATING EXPERIMENTAL RESULTS

METHOD FOR CALCULATING EXPERIMENTAL RESULTS

Data obtained experimentally during the gasification of char with steam included the volume of gas generated at 1-min time intervals and the composition of the gas at about 10-min time intervals. The following discussion illustrates the method used to determine the amount of char reacted.

Gas Compositions were determined by gas chromatography. The concentrations were normalized by:

$$X_i = \frac{X_{i\ (exp)}}{\Sigma X_{i\ (exp)}}$$

where X_i is the corrected mole fraction of component i and $X_{i(exp)}$ is the experimentally determined composition of component i, where i represents H_2, CO, CO_2, CH_4, N_2, O_2, C_2H_4, C_2H_6, and C_3H_8. For gasification with steam, i included only H_2, CO, CO_2, CH_4, and N_2.

The dry gas volume was determined from the wet gas volume by multiplication of the wet volume by a factor of 0.97 which represented the temperature and pressure conditions in the wet test meter.

Determination of the moles of C reacted was complicated by the carbonation and hydrolysis reactions that occurred in the melt. Early in some runs the following reaction was observed:

$$2NaOH + CO_2 \rightleftarrows CO + H_2$$

However, late in the run, the reverse of the above reaction occurred. Thus, simply determining the total $CO + CO_2 + CH_4$ in the gas was not sufficient for determining the carbon gasified. Therefore, the carbon gasified was determined from the H_2 content in the product gas that would be produced, or consumed, by the following reactions:

$$C + H_2O \rightleftarrows CO + H_2$$

$$C + 2H_2O \rightleftarrows CO_2 + 2H_2$$

$$C + 2H_2 \rightleftarrows CH_4$$

The concentration in the gas that represented carbon gasified was determined by the following:

$$(X_{CO} + X_{CO_2} + X_{CH_4})_c = X_{CO} + 1/2(X_{H_2} + 2X_{CH_4} - X_{CO}) + X_{CH_4}$$

The second term on the right hand side of the above equations represents the CO_2 concentration that would result if carbonation and hydrolysis of the melt were not occurring. The left hand side of the equation is the corrected sum of the CO, CO_2, and CH_4 concentrations used with the volume of gas generated to determine the amount of carbon reacted. The weight of carbon gasified was then determined by the following:

$$W_i - W = (X_{CO} + X_{CO_2} + X_{CH_4})_c \ (0.97)\ V\left(\frac{12}{24.4}\right)$$

where $W_i - W$ is the weight of carbon reacted, V is the wet test meter volume in liters, 0.97V is the dry volume, 12 represents the molecular weight of carbon and 24.4 represents the numbers of liters per g-mole of gas at conditions in the wet test meter.

The composition of the gas changed with time, and, therefore, required averaging of some type. The composition of a volume of gas generated over a given time interval was assumed to be the arithmetic average of the compositions at the beginning and end of the time interval. The gas generated at the start of a run was assumed to have all the composition determined by the initial in-line sample.

APPENDIX C

FLOWSHEET MASS AND ENERGY BALANCE CALCULATIONS

FLOWSHEET MASS AND ENERGY BALANCE CALCULATIONS

The following calculations were made to develop the material and energy balances shown in Figure 19; the numbers (below) refer to the stream number in that figure. The basis is a 200 ton/day plant with 10 wt% ferrous and bulk material segregated.

1. Weight of Material to Process = 0.9 (200 tons/day) = 180 tons/day

   - Proximate analysis same as for material used in study plus moisture to give 30 wt% moisture.
   - Percent fixed carbon for 30% moisture = 21 $(\frac{70}{95})$ = 15.5% where 21 was the experimentally determined fixed carbon in the refuse used in the study that had 95% dry material.
   - Ash content for 30% moisture = 14.2 $(\frac{70}{95})$ = 10.46%
   - Calorific value = 7202 Btu/lb $(\frac{70}{95})$ = 5350 Btu/lb
   - Total Energy Flow = $180 \frac{\text{ton}}{\text{day}} \times \frac{2000 \text{ lb}}{\text{ton}} \times \frac{1 \text{ day}}{24 \text{ hr}} \times \frac{5350 \text{ Btu}}{\text{lb}}$ =

     80.3×10^6 Btu/hr

2. Weight of Steam = $0.3 \times 180 \frac{\text{ton}}{\text{day}} \times \frac{\text{day}}{24 \text{ hr}} \times \frac{2000 \text{ lb}}{\text{ton}}$ = 4500 lb/hr

   - Scfm steam = $4500 \frac{\text{lb}}{\text{hr}} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{359 \text{ ft}^3}{18 \text{ lb}}$ = 1490 scfm
   - Energy content (steam release at 400°F) = 4500 lb/hr x 1171.9 Btu/lb = 5.3×10^6 Btu/hr
   - Composition of pyrolysis gas (from experiments):

	H_2	CO_2	C_2H_4	C_2H_6	CH_4	CO
Vol%	32.4	9.9	6.5	1.0	18.3	31.8
wt%	3.4	23.0	9.6	1.6	15.4	46.9

   - Avg. MW = 19

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- Volume gas generated = (0.64 ℓ/g from experimental studies)
- Volume gas at 180 ton/day = $0.64 \frac{\ell}{g} \times \frac{180\ (2000)\ lb}{24\ (60)\ min} \times \frac{453.6g}{lb} \times$

$$\frac{ft^3}{28.316\ell} \times (\frac{70}{95}) = 1890\ scfm$$

- Total flow = 3380 scfm (3400 scfm used for design)
- Potential heat flow in pyrolysis gas = $1890 \frac{ft^3}{min} \quad \frac{60\ min}{hr}$

$$\frac{540\ Btu}{ft^3} = 61.3 \times 10^6\ Btu/hr$$

- Sensible heat in pyrolysis gas (at 830°F)

$$= 0.506 \frac{Btu}{lb°F}\ (830\text{-}77)°F\ 1890 \frac{ft^3}{min}$$

$$\frac{60\ min}{hr} \quad \frac{19\ lb}{359\ ft^3}$$

$$= 2.3 \times 10^6\ Btu/hr$$

- Total energy in wet pyrolysis gas = $2.3 + 61.3 + 5.3) 10^6 =$

$$68.9 \times 10^6\ Btu/hr$$

3. Char Production Rate = $\frac{180\ (2000)}{24}$ lb/hr x 0.155 = 2325 lb/hr
   - Combustion gas composition: 10% CO, 15% CO_2, 75% N_2
   - Air required = $2325 \frac{lbC}{60\ min} \quad \frac{1\ lb\ mole\ C}{12\ lb\ C} \quad \frac{20\ lb\ mole\ O_2}{25\ lb\ mole\ C}$

$$\frac{359\ ft^3\ air}{0.21\ lb\ mole\ O_2} = 4420\ scfm$$

4. Same Air Flow = 4420 scfm
   - Sensible heat at 700°C = $\frac{0.27\ Btu}{lb\ °F} \times 675\ (1.8)°F \times$

$$\frac{4420(60)ft^3}{hr} \times \frac{28.8\ lb}{359\ ft^3} = 7 \times 10^6\ Btu/hr$$

5. Combustion Gas Flow Rate = 4420 (1.05) scfm = 4640 scfm
   - Calorific value = $0.1\ (4343.6\ Btu/lb \frac{28\ lb}{359\ ft^3}) = 33.9\ Btu/ft^3$
   - Potential heat = 33.9 (4640) 60 Btu/hr = 9.4×10^6 Btu/hr

- Sensible heat at 700°C = 0.27 Btu/lb°F (675) 1.8°F

$$\frac{4640\ ft^3\ (60)}{hr}\ \frac{30.3\ lb}{359\ ft^3} = 7.7 \times 10^6\ Btu/hr$$

- Total heat = $(9.4 + 7.7)10^6$ Btu/hr = 17.1×10^6 Btu/hr

6. Secondary Combustion Air Requirements =

$$(0.1)4640\ \frac{ft^3}{min}\ \ CO \times \frac{1\ ft^3\ O_2}{2\ ft^3\ CO} \times \frac{ft^3\ air}{0.21\ ft^3\ O_2} = 1105\ scfm$$

- Use a 20% excess
- Secondary combustion air flow, 20% excess = 1.2 x 1105 scfm = 1330 scfm
- Temperature = 25°C
- Heat Content = 0

7. Air Flow From Secondary Combustion = (4640 + 1330 - 480) scfm = 5490 scfm

$$\Delta T = \frac{17.1 \times 10^6\ Btu}{60\ min} \times \frac{1\ min}{5490\ ft^3} \times \frac{lb°F}{0.27\ Btu}\ \frac{359\ ft^3}{31\ lb} =$$

2226°F

= 1237°C

T = 1260°C

- Heat Content = 1237 (1.8)°F x 0.27 $\frac{Btu}{lb°F}$ x $\frac{5490(60)ft^3}{hr}$ x $\frac{31\ lb}{359\ ft^3} = 17.1 \times 10^6$ Btu/hr

8. Air Flow from Secondary Combusion after Heat Exchange =

5490 scfm T = 750°C

- Heat content = 725 (1.8)°F x 0.27 $\frac{Btu}{lb°F}$ x $\frac{5490(60)ft^3}{hr}$ x $\frac{31\ lb}{359\ ft^3}$

= 10.1×10^6 Btu/hr

9. Ash - slurry flow =

$$\frac{180 \text{ ton refuse}}{\text{day}} \times \frac{10.46 \text{ ton ash}}{100 \text{ ton refuse}} \times \frac{\text{ton slurry}}{0.25 \text{ ton ash}} = 75.3 \text{ ton/day}$$

- Volume flow = $\frac{75.3(2000) \text{ lb}}{24 \text{ hr}} \quad \frac{\text{ft}^3}{2.25(62.4)\text{lb}} = 44 \text{ ft}^3/\text{hr}$

  T = 900°C

- Heat content in salt = $\frac{75.3(0.75)(2000)}{24} \quad \frac{\text{lb salt}}{\text{hr}}$

  $50(1.8)°F(0.437 \frac{\text{Btu}}{\text{lb°F}}) + 118.9 \frac{\text{Btu}}{\text{lb}} + 825(1.8°F)0.273$

  Btu/lb°F = 2.7×10^6 Btu/hr

- Heat content in ash = $\frac{75.3(0.25)(2000) \text{ lb ash}}{24 \text{ hr}} \times$

  $875(1.8°F)0.4 \frac{\text{Btu}}{\text{lb°F}} = 1 \times 10^6$ Btu/hr

- Total heat flow 3.7×10^6 Btu/hr

10. Ash-Salt Discharge = $0.25(75.3) \frac{\text{ton ash}}{\text{day}} + 0.04(75.3)0.75$

$$\frac{\text{ton salt}}{\text{day}} = 21.1 \text{ ton/day (with 4\% salt loss)}$$

- T = 25°C
- Heat content = 0

11. Recovered Salt = $0.75(75.3) \frac{\text{ton salt}}{\text{day}} \quad (0.96) = 54.3 \frac{\text{ton salt}}{\text{day}}$

- T = 25°C
- Heat content = 0

12. Required Recycle Salt = $75.3(0.75) \frac{\text{ton salt}}{\text{day}} = 56.5 \frac{\text{ton salt}}{\text{day}}$

- T = 900°C
- Heat content in salt = $\frac{75.3(0.75) \text{ 2000 lb salt}}{24 \text{ hr}}$

  $\frac{0.273 \text{ Btu}}{\text{lb°F}} \quad (825)1.8°F + 118.9 \text{ Btu/lb} + 50(1.8)°F$

  $(0.437 \frac{\text{Btu}}{\text{lb°F}}) = 2.7 \times 10^6$ Btu/hr

13. Makeup Salt = (56.5 - 54.3) ton/day = 2.2 ton/day

- T = 25°C
- Energy Content = 0

14. Heat Addition Required to Melt Recycle Salt = 2.7×10^6 Btu/hr

- T - 900°C
- Heat content in salt = $\frac{75.3(0.75)2000 \text{ lb salt}}{24 \text{ hr}}$

$$\frac{0.273 \text{ Btu}}{\text{lb°F}} (825) 1.8°F + 118.9 \text{ Btu/lb} + 50(1.8)°F$$

$$(0.437 \frac{\text{Btu}}{\text{lb°F}}) = 2.7 \times 10^6 \text{ Btu/hr}$$

15. Heat Loss in Salt Recovery Operation = 3.7×10^6 Btu/hr

(Same as in Item 9)